Lecture

# Nanoceramics

## An Overview of Nano Materials

Prof. Dr. Julian Plewa
Dr. Florian Baur

Fachhochschule Münster University of Applied Sciences

Material Sciences
Dept. of Chemical Engineering

# Literature

**The Chemistry of Nanomaterials: Synthesis, Properties and Applications, 2 volumes** *C. N. R. Rao, A. Müller, A. K. Cheetham (Eds.), Wiley, 2004*

**Nanoparticles: From Theory to Applications**
*G. Schmid (Ed.), Wiley, 2004*

**Nanotechnologie,** *R. Clasen, Univ. Saarlands SS2011*

**Raport nanoROAD** Overview on Promising Nanomaterials for Industrial Applications", **October 2005**.

**A Review of the Emerging Nanotechnology Industry: Materials, Fabrications, and Applications,** *Hai-Yong Kang, 2010*

http://www.nano.gov
http://www.understandingnano.com
http:// www.nanotechproject.org/inventories/medicine
http://www.nanomedjournal.com
http://www.nanowerk.com

# Definitions

**Nano material:**

„A **natural, incidental or manufactured material** containing particles, in an unbound state or as an aggregate or as an agglomerate and **where**, for 50% or more of the particles in the number size distribution, **one or more external dimensions is in the size range 1 nm - 100 nm**."

European Commission (18 October 2011)

**Nano ceramic:**

Ceramic materials **comprised** of particles of 100 nm or less, i.e. **of nano materials**.

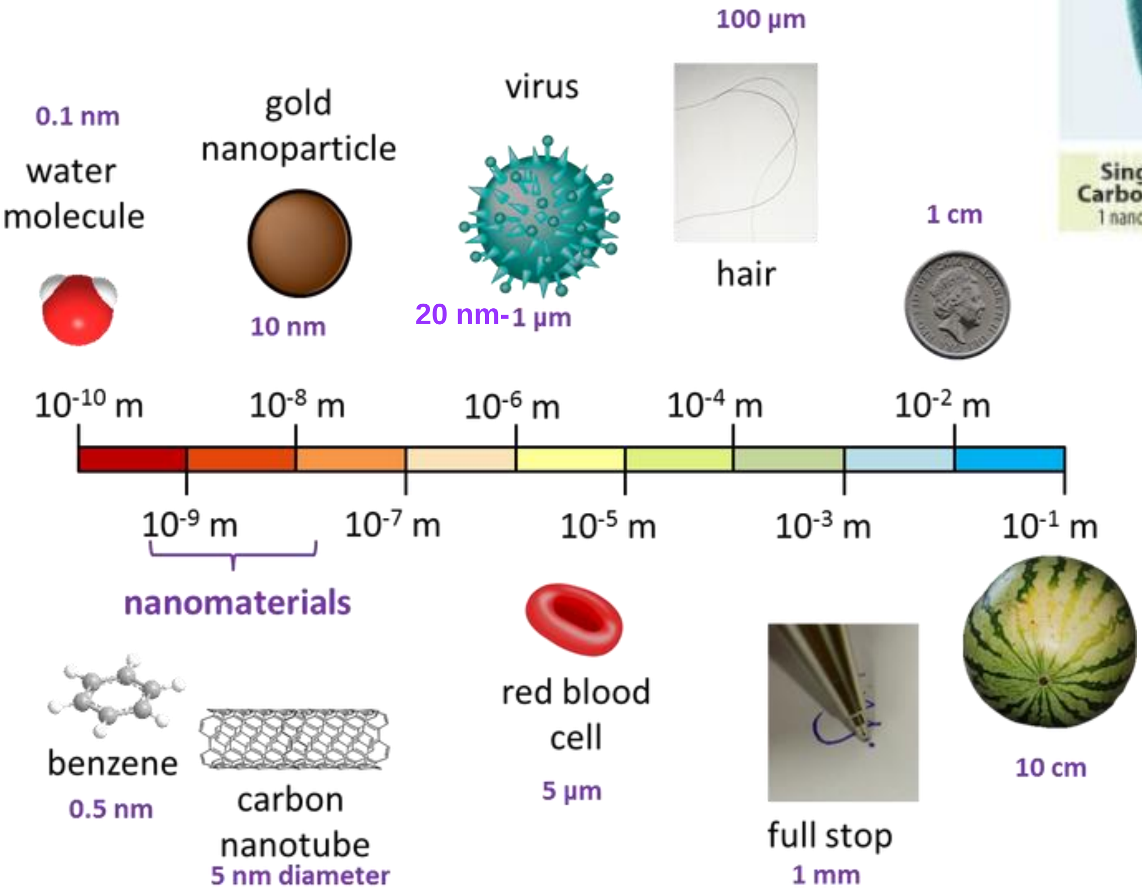
# Lecture

## Parts:

- **Overview of Nano Materials**
- Ceramics
- Fabrication of Nano Materials
- Phenomena in Dispersed Systems
- Consolidation of Nano Powders
- Propertes of Nano Ceramics

# Overview of Nano Materials

***„nano to macro“***

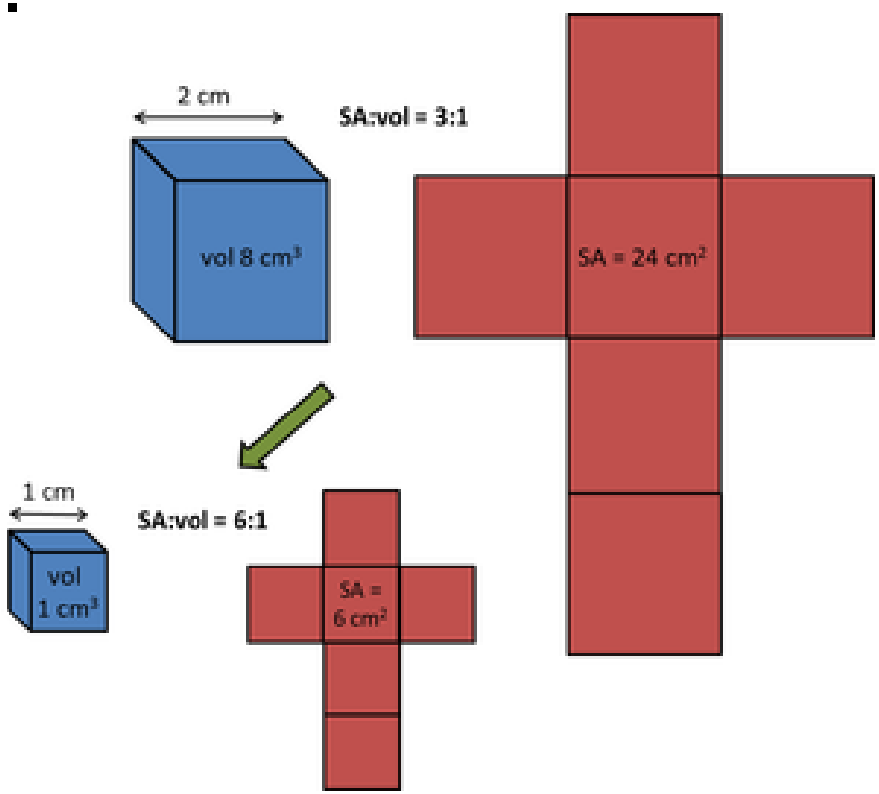




https://chembam.com/definitions/nanotechnology/

# Overview of Nano Materials

**Surface-to-Volume ratio increases with decreasing size:**




**Material properties can change drastically:**

- **Melting point**
- **Magnetic properties**
- **Color**
- **Conductivity**

**…**

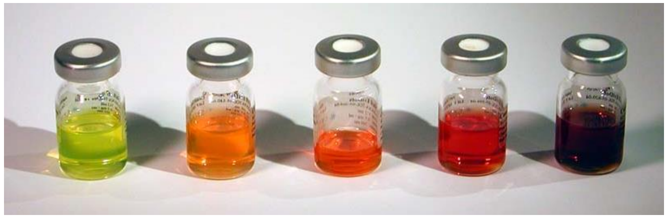
**These changes can appear suddenly**

**https://chembam.com/definitions/nanotechnology/**

# Overview of Nano Materials

- Cluster in Inorganic Chemistry - Narrow Definition:
  Compounds with metal-metal bonds with at least 3 metal atoms

- Cluster – Extended Definition
  Small groups of atoms (often used for metal oxides)



- Nanoparticles
  Particle with nano-dimensions

**Quantum dots are clusters of ~$10^4$ atoms with specific optical properties**

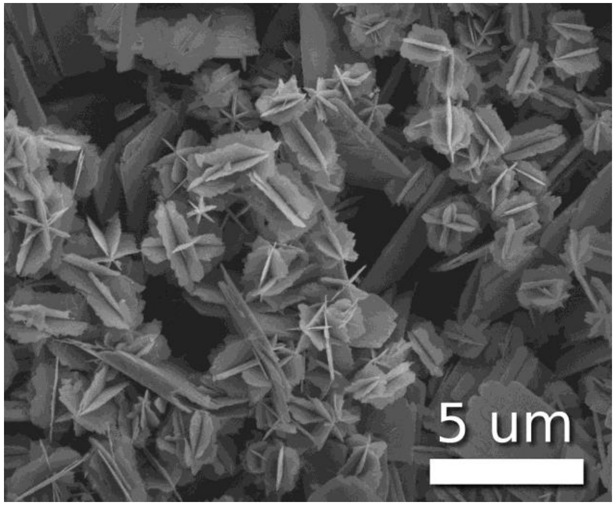
Prof. Dr. Plewa
Dr. Baur

# Overview of Nano Materials

## Categorization:

***Nano-object:***

**a material with one, two, or three external dimensions with a size of approximately 1 - 100 nm**




**$VO_2$ nanoparticles**

- ***Nanoplate***
  - **one nm-scale dimension**
  - **Graphene, silicate clay (montmorillonite)**

- ***Nanofiber, nanotube, nanorod***
  - **two nm-scale dimensions**
  - **cellulose, poly(lactic acid), carbon nano-tubes, gold**

- ***Nanoparticle***
  - **three nm-scale dimensions**
  - **$TiO_2$, $SiO_2$, …**

# Overview of Nano Materials

## Nano technology comprises:

-Nano electronics

**Nano technology is a highly interdisciplinary field!**

-Nano medicine

-Nano machines

**-Nano materials (such as nano ceramics)**

# Overview of Nano Materials

**Examples for application:**

Functionalisation of surfaces: „self-cleaning“ surfaces

Catalysis, chemistry and materials science: catalytical nano particles

Energy transformation and storage: carbon nano tubes as hydrogen storage

Construction: reinforcement of building materials

Sensors and actuators: Lab-on-a-Chip, logic and memory units

Life sciences: Improving medical diagnosis, therapy pathways (cancer treatment, wound care)

Defense: sensors for damage detection, water repellent uniforms

Automotive industry: nano particles as fuel additives

Aviation: low-weight, durable and temperature resistant coatings

# Overview of Nano Materials

**Selected packaging materials that contain nano materials [Öko-Institut, TA-SWISS** ]:

| **Product** | **Substance** | **Composition** | **Application** |
|---|---|---|---|
| Packaging (Bayer) | Clay mineral (silicate) | Nano particles in polymer | Bottles, foils |
| Packaging (Honeywell) | Clay mineral (silicate) | Nano particles in polymer | Bottles with oxygen scavanger |
| Packaging (Nanocor) | Clay mineral (silicate) | Nano particles in polymer | Bottles |
| Packaging (Plantic) | Clay mineral (silikate) | Nano particles in bio degradable polymer | Trays |

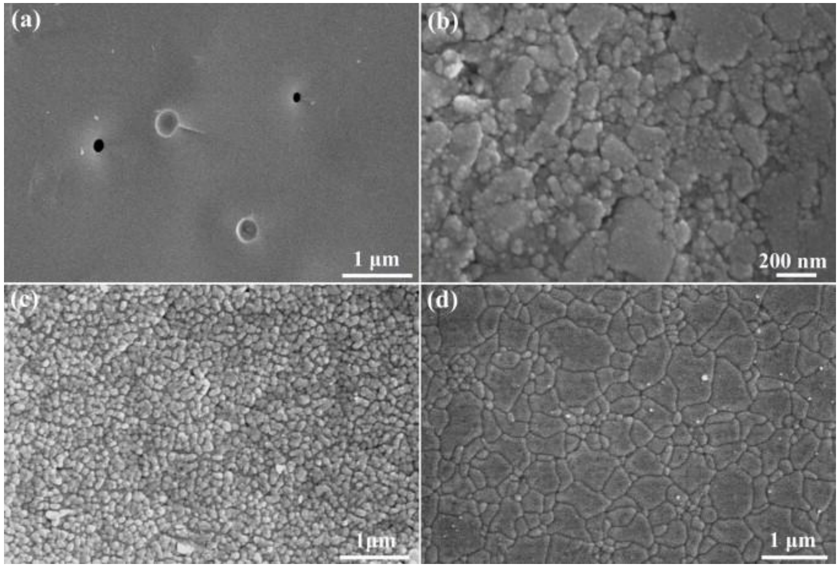
**Embedded nano particles increase:**
**flame retardancy, thermal stability, peak heat release rate, fracture, and strength**

# Overview of Nano Materials

**Nano ceramics are a part of nano technology:**

**→ nano scale ceramics where at least one dimension is in nano scale, e.g. nano particles, fibers, tubes, rods, foils**

**→ macro scale ceramics made from nano scale particles**




**SEM images of the $(Y_{0.94}Gd_2)O_5O_{12}:Ce_{0.06}$ bulk samples heat-treated at different temperatures (a) glass hot-pressed at 910 °C, (b) 1100 °C, (c) 1200 °C, (d) 1400 °C.**
**Mater. Res. Bull. 66 (2015) 45**

# Overview of Nano Materials

**Powder:**

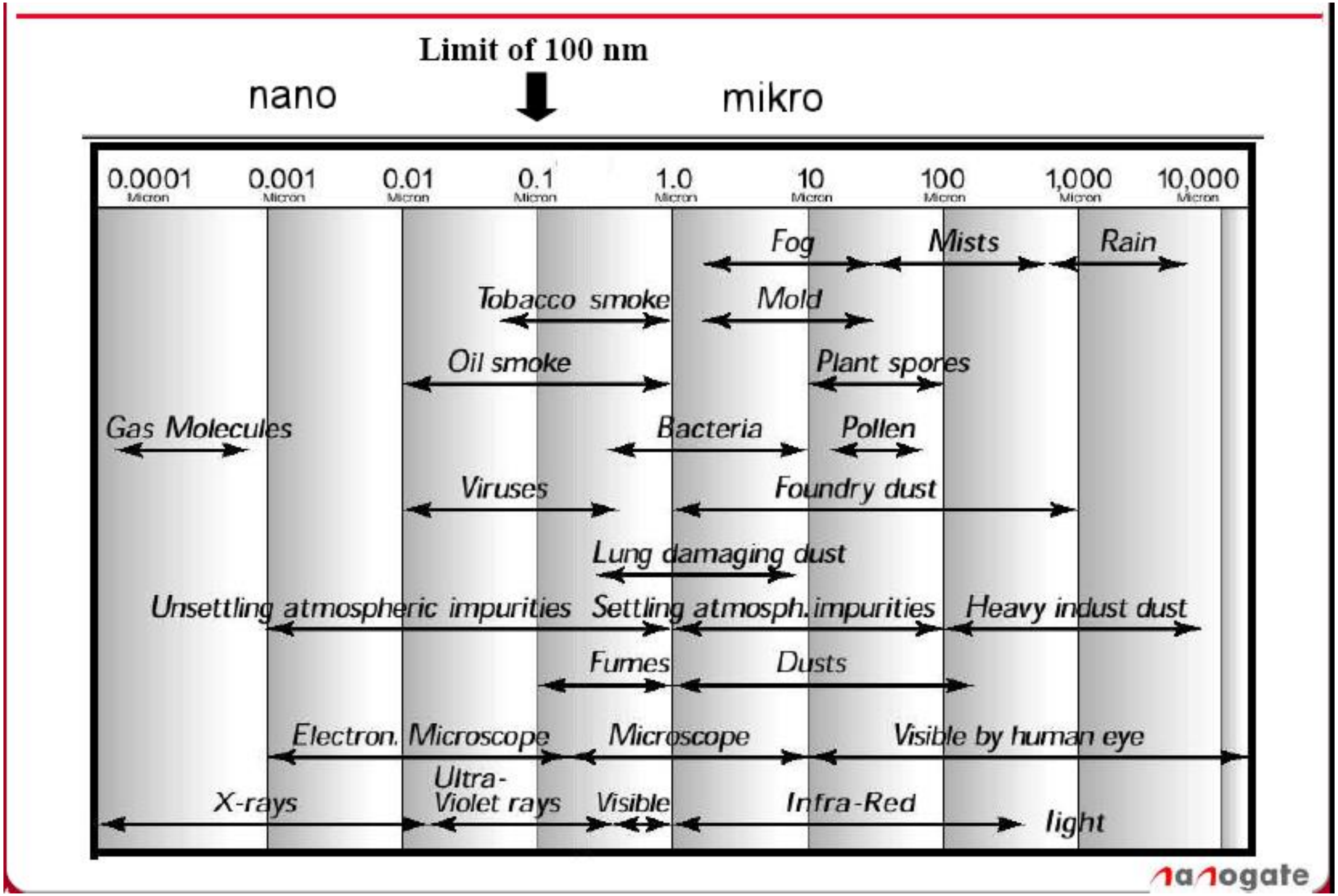
- **consists of a large number of freely moveable particles**
- **dry**
- **particles are loosely contacted**
- **flow properties depend on the morphology and electrostatic charge**

# Overview of Nano Materials

## Classification of solid matter by particle size:

| Diameter (µm) | Name | Parts |
|---|---|---|
| < 0.1 | nano powder | particles |
| 0.1 - 1 | ultra fine powder | particles |
| 1 - 10 | super fine powder | particles |
| 10 - 100 | granular powder | particles |
| 100 - 3000 | granular solid | granules |
| 3000 - 10000 | fragments | grains |

# Overview of Nano Materials



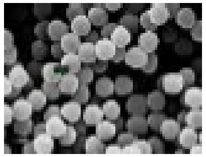

Prof. Dr. Plewa
Dr. Baur

# Overview of Nano Materials

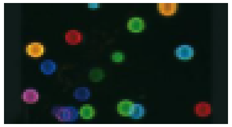
Typical size of some nano-scale materials [Rao et al., 2004].

| Form | Size | Material |
|---|---|---|
| Nanocrystals | Diameter of 1…10 nm | Metals, semiconductors, magnetic materials. |
| Nanowires | Diameter of 1…10 nm | Metals, semiconductor, oxides sulfides, nitrides. |
| Nanotubes | Diameter of 1…10 nm | Carbon, layered metal. |
| Nanoporous solids | Pore diameter of 0.5…10 µm | Zeolites, phosphates, etc. |
| 2-dimensional array | Several $nm^2$…$\mu m^2$ | Metals, semiconductors, magnetic materials. |
| Surface and thin film | Thickness 1…1000 nm | Variety of materials. |
| 3-dimensional structures (super lattices) | Several $nm^3$…$\mu m^3$ | Metals, semiconductors, magnetic materials. |

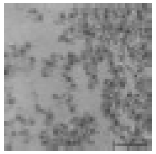
# Overview of Nano Materials



| | |
|---|---|
| Titanium dioxide | UV absorber, photo catalyst |
| Zinc oxide | UV absorber |
| Silicon dioxide | hardness or to increase flow |



| | |
|---|---|
| Gold | polychrome, catalyst |



| | |
|---|---|
| Iron oxide | supramagnet, catalyst |

| | |
|---|---|
| Carbon nano fibres | increases mechanical stability<br>low weight |

SRU

Prof. Dr. Plewa
Dr. Baur

# Overview of Nano Materials

nanocrystalline materials
metals, intermetallics, ceramics and composites.

Nano materials

| Metals | Ceramics | Composite |
|---|---|---|

Nano and micro materials

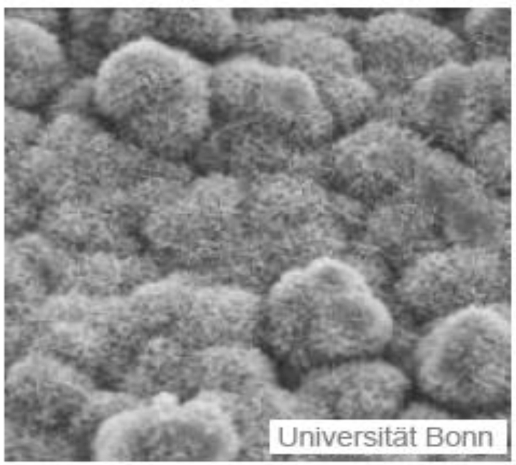
| Metals and ceramics | Plastics and ceramics |
|---|---|

Prof. Dr. Plewa
Dr. Baur

# Overview of Nano Materials

Metallic nano particles

e.g. Pt-, Au-, Cu-  nano particles




Künstlich strukturierte Oberflächen, z.B. galvanisch hergestellte, metallische Kupferfolie, überzogen mit feinsten Nanonadeln

**Lycurgus cup (roman) contains Au and Ag nano particles.**

**Green color: light scattering by Ag**
**Red color: light absorption by Au**

Lycurgus-Kelch aus dem Britischen Museum (4. Jhr. Nach Christus): Links in Auflicht, rechts in Durchlicht aufgenommen.
http://www.expeditionzone.com/start_hi.cfm?story=2370&business=&club=&member=

Prof. Dr. Plewa
Dr. Baur

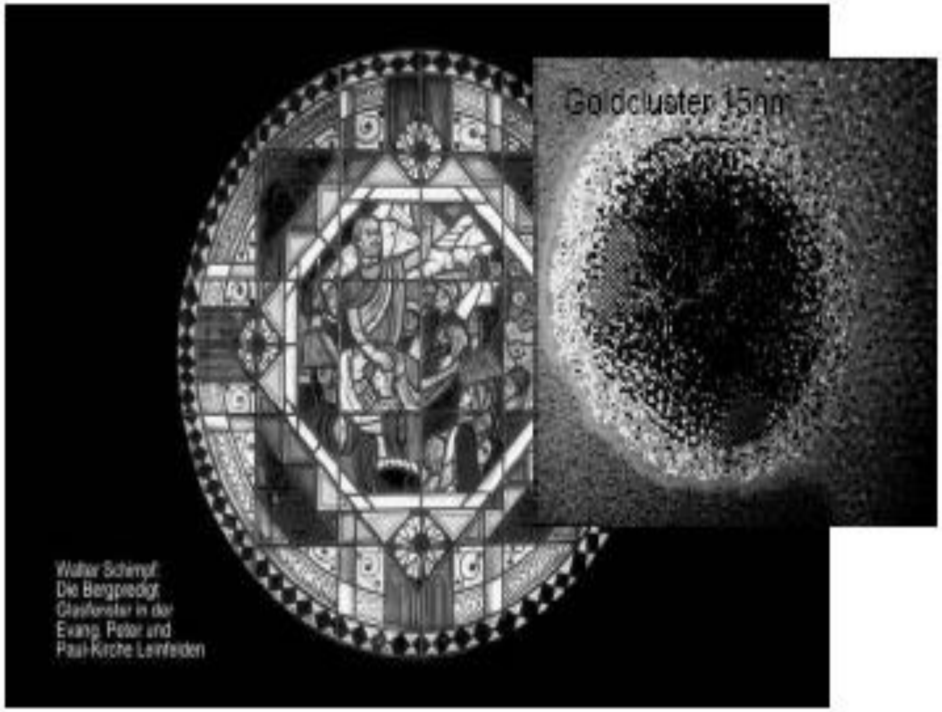
# Overview of Nano Materials

## Metallic nano particles

Au nano particles

(Norwich, England, ca. 1480).

The ruby color is probably due to embedded gold nanoparticles




**Long-term stability of nano particles in glass**

Prof. Dr. Plewa
Dr. Baur

# Overview of Nano Materials

## Carbon nano particles

**Damascus steel**

Investigation via SEM showed the structure of damascus steel:

Cementite ($Fe_3C$) nanowires and carbon nanotubes are present in the steel. The patterns are caused by cementite grains on the surface.

The combination of metallic iron, cementite and carbon nanotubes results in superior properties of the steel.


Nano technology was used centuries ago without being aware of it

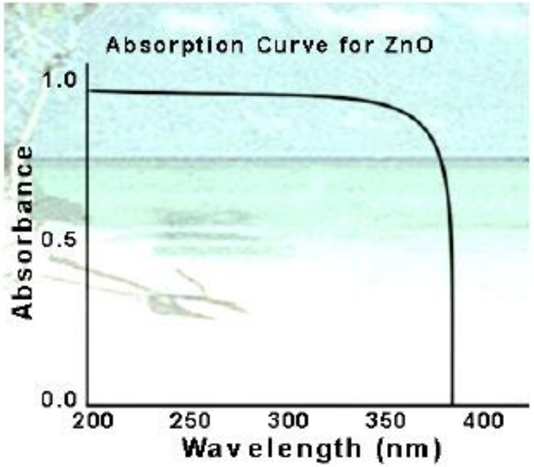
Prof. Dr. Plewa
Dr. Baur

# Overview of Nano Materials

## Ceramic nano materials

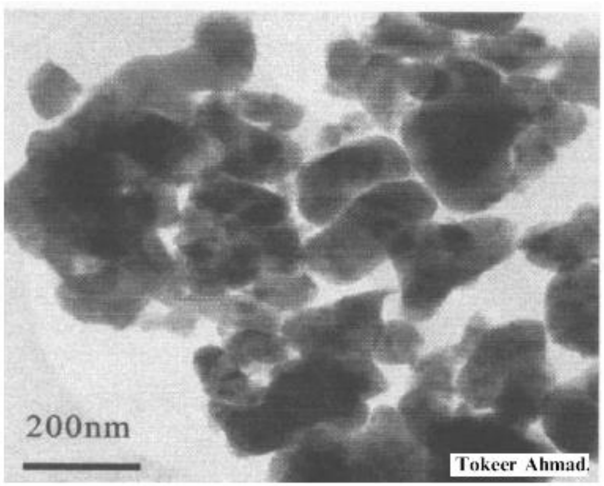
e.g. $SiO_2$, $Al_2O_3$, $TiO_2$, ZnO, $Mn_3O_4$

White pigment:

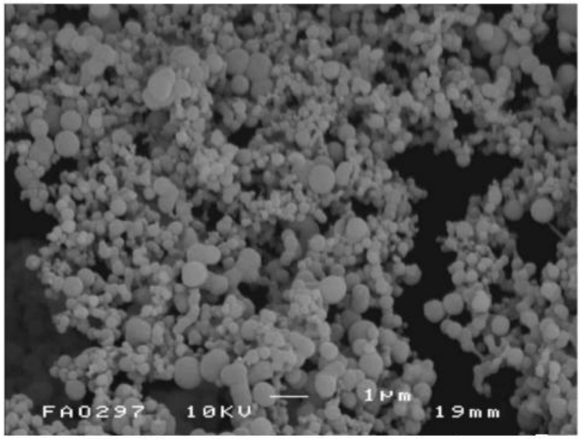



Functional materials

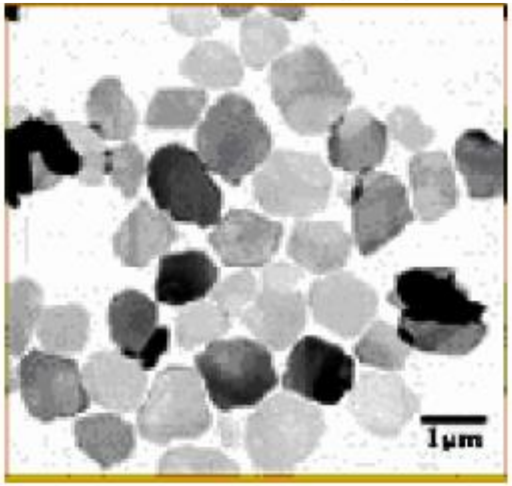
$TiO_2$ nano particles
with Rutil structure




TEM micrograph of $Mn_3O_4$ nanoparticles.




*SEM images of the 'as precipitated' nanopowder (mean particle size = ca 280 ± 68 nm, sample of 103 particles)* [J.A. Darr]




ZnO powder dispersion in a sunscreen (courtesy Elta Block).


Prof. Dr. Plewa
Dr. Baur

# Overview of Nano Materials

## Ceramic nano materials

e.g. $SiO_2$, $Al_2O_3$, $TiO_2$, ZnO, $Mn_3O_4$

Oxidic nano particles:
Pigments, ceramics, membranes, structured catalysts, micro batteries

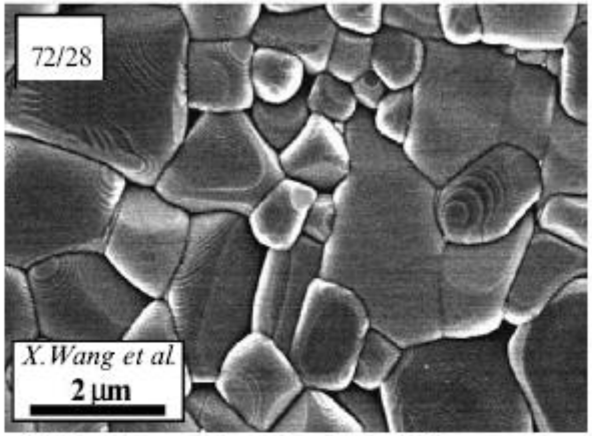
$SiO_2$, $Al_2O_3$, $CeO_2$ nano particles:
polishing

$TiO_2$ and ZnO nano particles:
UV absorber

$V_2O_5$ and $TiO_2$ nano particles:
catalysis

$Al_2O_3$, $TiO_2$ nano ceramics

Construction

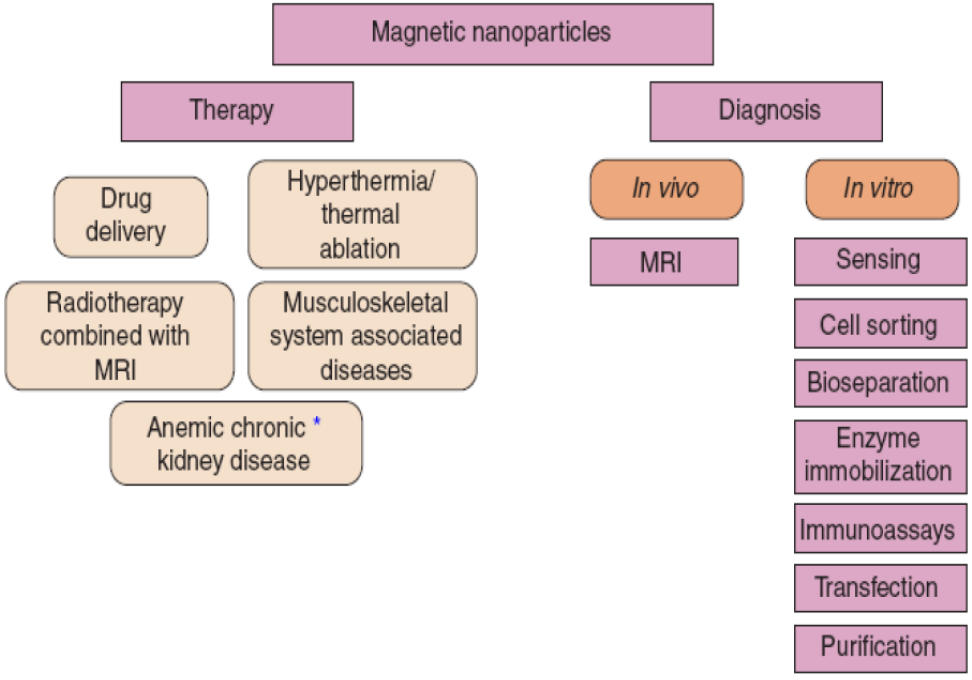



SEM micrographs of polished CG ceramic.
CG: 72/28 $Al_2O_3/Al_2TiO_5$

Prof. Dr. Plewa
Dr. Baur

# Overview of Nano Materials

## Magnetic nano materials




applications of magnetic nanoparticles (NPs)


Prof. Dr. Plewa
Dr. Baur

# Overview of Nano Materials

## Magnetic nano materials

### MAGNETIC NANOPARTICLES

Magnetic ceramic nanoparticles

the location and detection of viruses: a viral nanosensor.

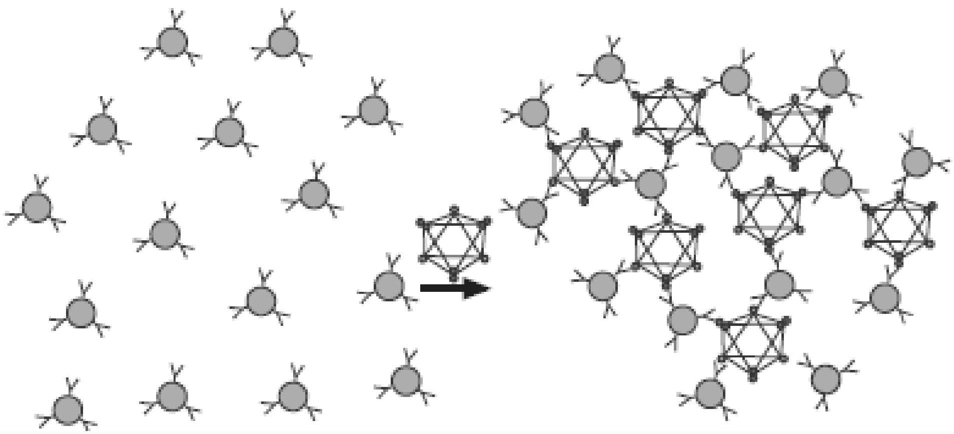


Diagram of a viral-induced nanoassembly of magnetic nanoparticles.

Iron oxide particles (~50 nm in diameter) with a dextran coating are covered with antibodies. The antibodies are chosen for a specific virus (e.g., herpes simplex virus or adenovirus). When these specially coated nanoparticles are then exposed to the virus they will form clusters that would be large enough to be visible on a nuclear magnetic resonance (NMR) or magnetic resonance imaging (MRI) scan. This approach has already been demonstrated in the laboratory using viral particles in solution. The idea is that it might eventually be used to detect viruses in human body fluid or tissue.

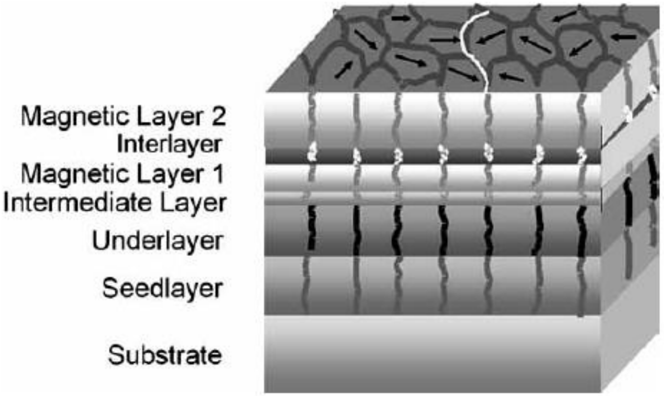
Prof. Dr. Plewa
Dr. Baur

# Overview of Nano Materials

## Composites

- Nano-composite: mixture of different materials on nanoscale

for example: Co, Cr, Pt, $SiO_2$

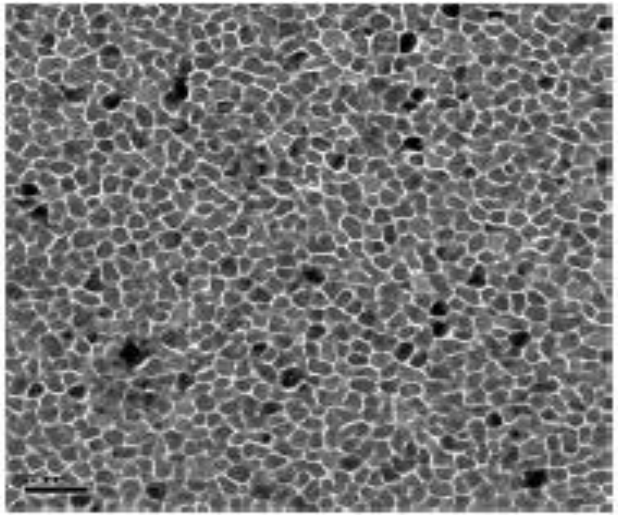



magnetic recording medium.
ferromagnetic layer separated by a nonmagnetic interlayers

recording media

thin films of several layers sputtered onto a substrate.
(Al alloys or glass, thickness from 0.35 mm to 2mm)
few magnetic layers – CoCrPt alloys with $SiO_2$

recording media material: Co grain;30 nm
CoCrPt alloys with $SiO_2$ or thin oxide



TEM image of a granular perpendicular recording medium. The grains are separated from each other by a thin oxide region. (Black lines illustrate the bit boundary) [Rachid Sbiaa]

Prof. Dr. Plewa
Dr. Baur

# Overview of Nano Materials

## Composites

**Increasing hardness**

Nano-composite: mixture of different materials on nanoscale

**Metallic nano particles in alloys**

Dispersion hardening – nano particles are diffused into a metal to increase hardness

e.g. Co in Cu
Cu in Al

**Oxide and non-oxide ceramics in alloys**

Light metals (Al, Mg) + carbides ($B_4C$, SiC), nitrides (BN, AlN), borides ($TiB_2$), oxides ($Al_2O_3$)

ceramic/metal composites

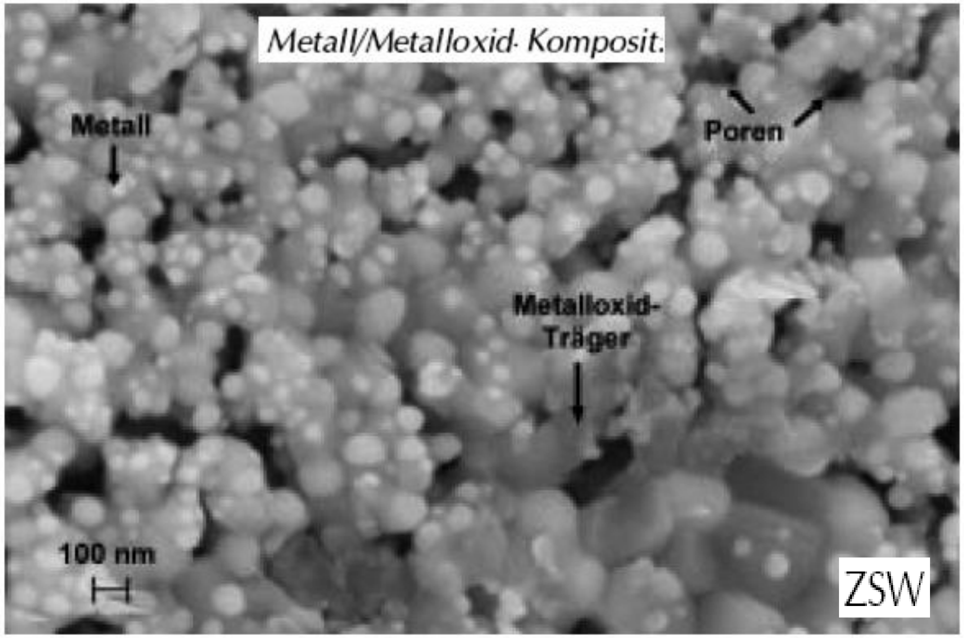
High strength steel: Carbide precipitates with diameter of < 10 nm

Prof. Dr. Plewa
Dr. Baur

# Overview of Nano Materials

## Composites

·Nano-composite: mixture of different materials on nanoscale




nanoporösem Metalloxidträger – belegt mit Metallpartikeln

Metal / metal oxide composite:

a porous oxidic base is covered with metallic particles with a size of 40-100 nm

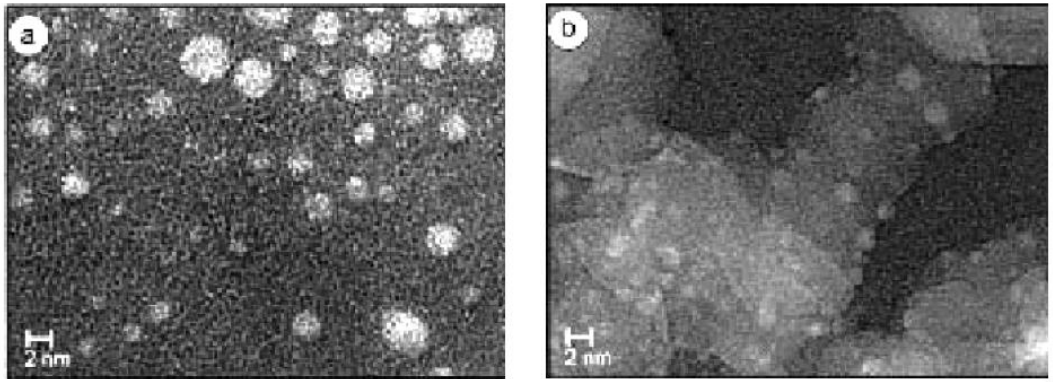
Application: catalysis


Prof. Dr. Plewa
Dr. Baur

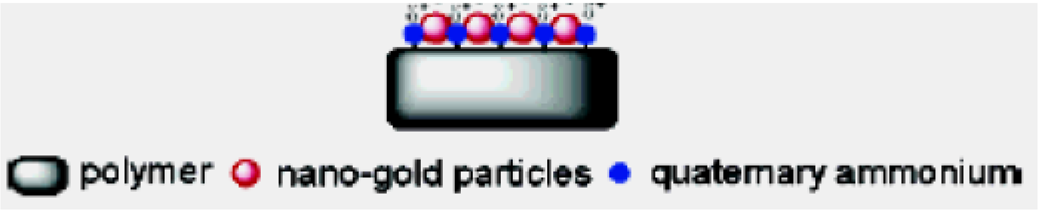
# Overview of Nano Materials

metallic nano particles with ceramic micro particles

e.g. Pt or Au nano particles on the matrix

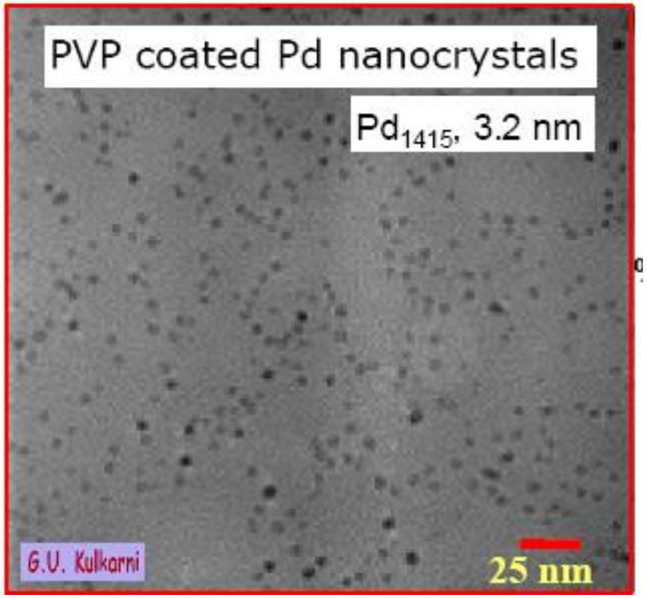


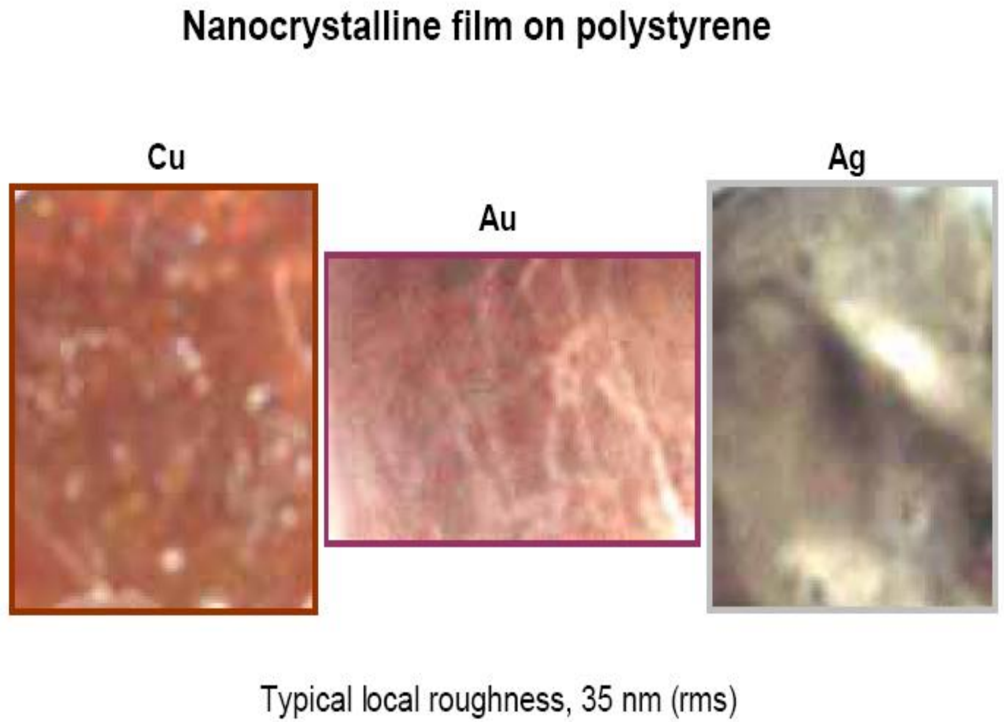

Gold cluster on an oxidic base



# Overview of Nano Materials

metallic nano materials with polymers

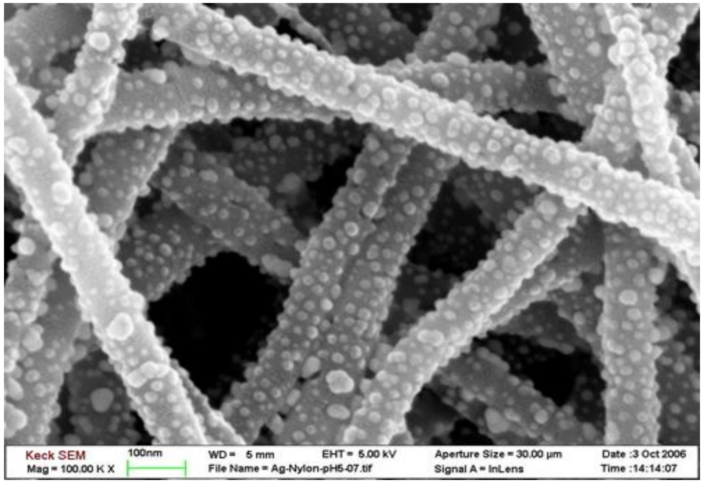



Prof. Dr. Plewa
Dr. Baur

# Overview of Nano Materials

## metallic nano particles with polymers




Anti-Bacterial
FE-SEM: Zeiss(1550)-Clark
This image shows electrospun nylon 6 nanofibers decorated with surface bound Ag nanoparticles.

Immersing nylon 6 nanofibers into Ag colloidal solution with pH 5, Ag nanoparticles were assembled onto nylon 6 nanofibers via interaction between nylon 6 and protection groups of Ag nanoparticles. Future applications include antibacterial filtration.

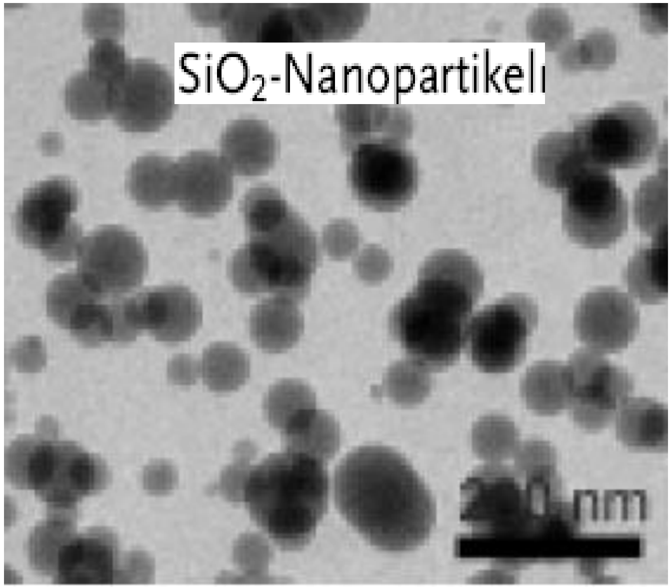
Fiber Science and Apparel Design (Hong Dong)

# Overview of Nano Materials

## ceramic nano particles with polymers

e.g. MgO, $Al_2O_3$ or $SiO_2$ nano particles or carbon nanotubes as fillers in PE

$SiO_2$ nano particles are used as *thickening agents*, *fillers* or to increase mechanical toughness




Prof. Dr. Plewa
Dr. Baur

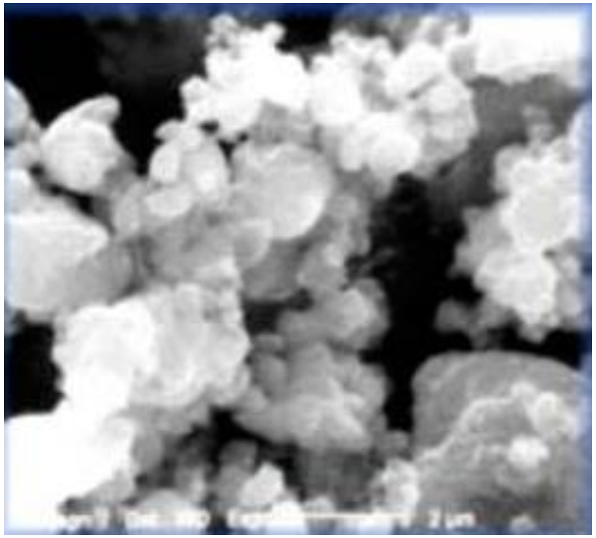
# Overview of Nano Materials

ceramic nano particles with ceramic micro particles

$SiO_2$ nano particles as filler in concrete:

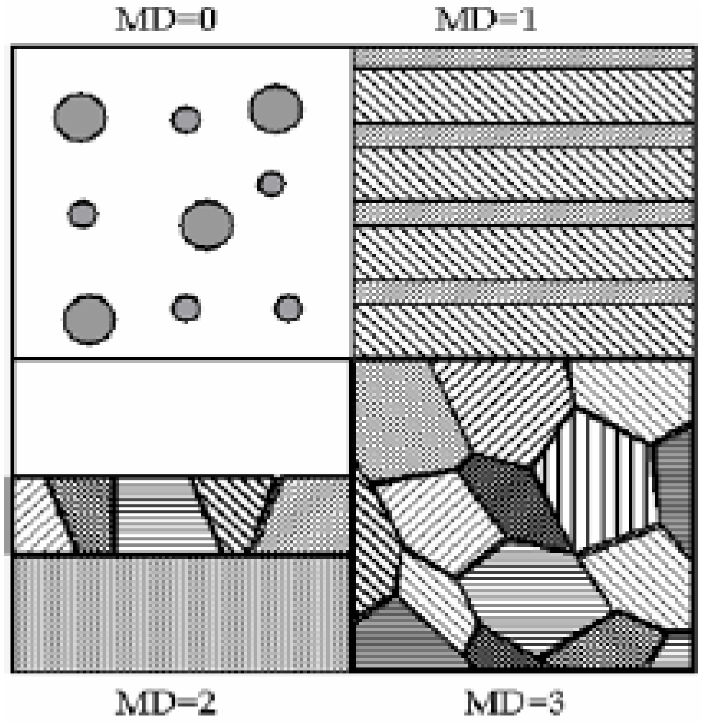
The amount of micro pores is decreased,
this results in an increased hardness.

nanostructured matrix for
the solid lubricant in
combination with
nanophased powder



# Overview of Nano Materials

## Siegel classification of nano materials




Definition of nanomaterials following Siegel

Siegel classification:

- Clusters or powder (MD=0)
- Multi layers (MD=1)
- Ultra-thin grainy films (MD=2)
- Composites (MD=3)

# Overview of Nano Materials

## Siegel Classification

Dimension 0 — zero-dimensional atom clusters.

Dimension 1 — one-dimensional modulated multilayers

Dimension 2 — two-dimensional ultra-fine- grained overlayers.

Dimension 3 — three-dimensional nanocrystalline structures

A nanoparticle is a quasi-zero-dimensional (**0D**) nano-object in which all characteristic linear dimensions are of the same order of magnitude (not more than 100 nm).

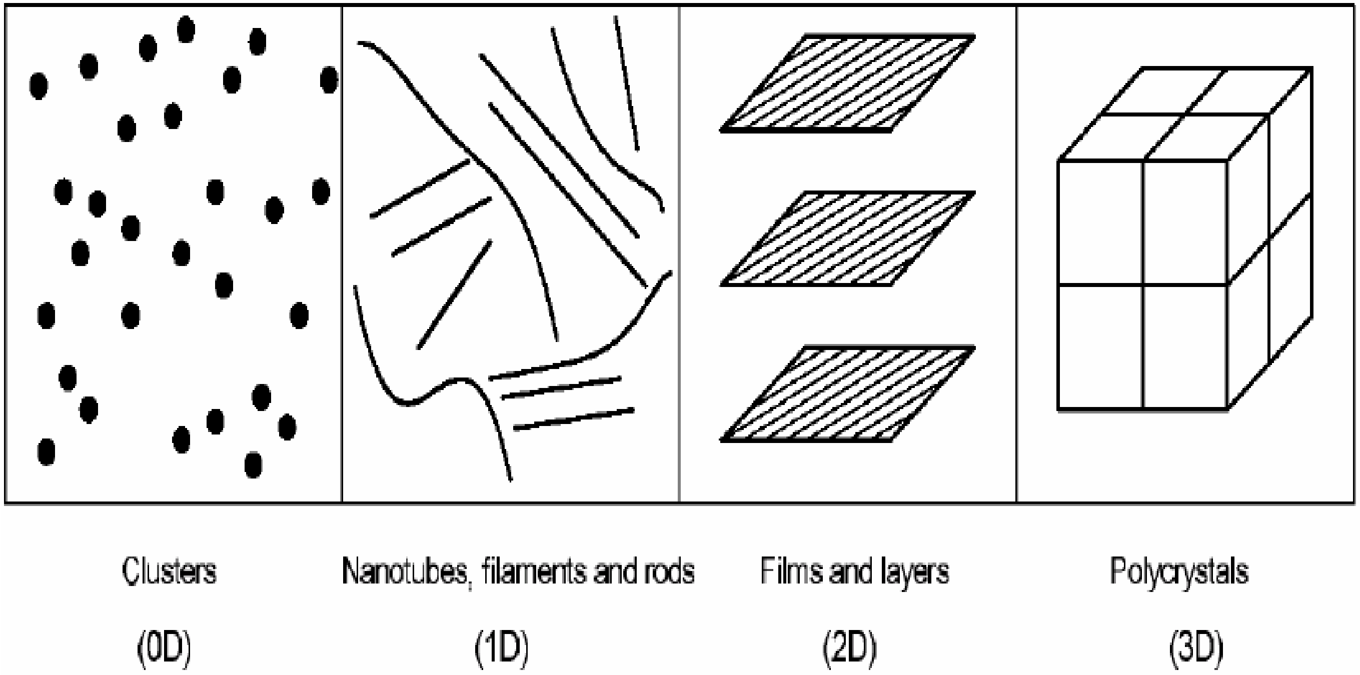
Nanorods and nanowires are quasi-one-dimensional (**1D**) nano-objects.

The group of two-dimensional objects (**2D**) includes planar structures, nanodiscs, thin-film magnetic structures, magnetic nanoparticle layers, etc., in which two dimensions are an order of magnitude greater than the third dimension, which is in the nanometre range.

Nanocrystalline materials can be classified into several groups according to their dimensionality: zero-dimensional atom clusters, one-dimensional modulated multilayers, two-dimensional ultra-finegrained overlayers, and three-dimensional nanocrystalline structures

# Overview of Nano Materials

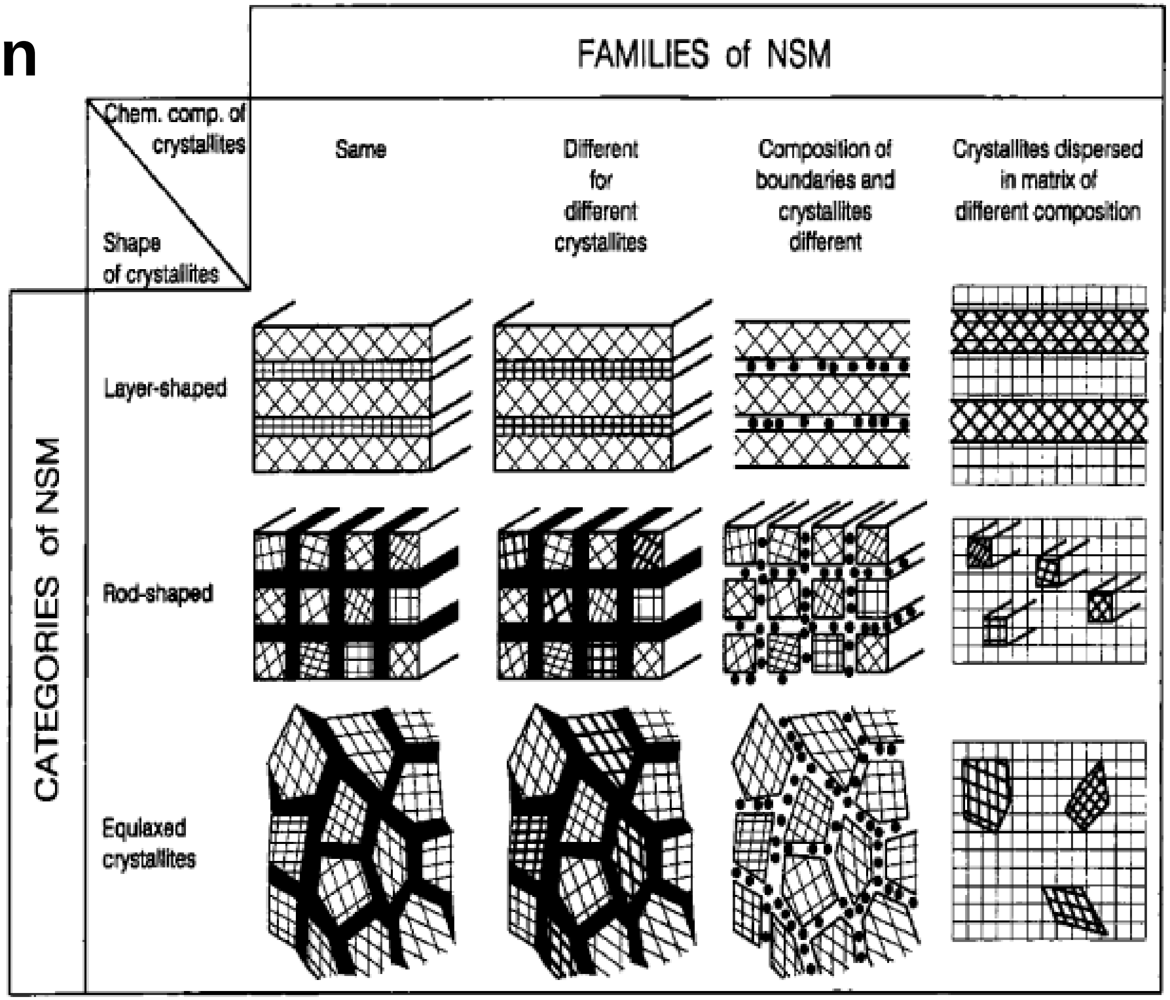
## Siegel classification



# Overview of Nano Materials

## Gleiter classification

Classification schema for nanocrystalline materials according to their chemical composition and the dimensionality (shape) of the crystallites (structural elements) forming the materials



# Overview of Nano Materials

**Specific surface area of nano materials**

Prof. Dr. Plewa
Dr. Baur

# Overview of Nano Materials

## Specific surface area

A large fraction of the atoms of a nano particle are surface atoms:

Diameter: 10 nm

Number of atoms: 30 000

Fraction of atoms on surface: 20%

At **5 nm diameter 40%** are on the surface, at **2 nm 80%** and at **1 nm 99%**!

- **melting point decreases**
- **defect density increases**
- **crystal structure can change**
- **band gap changes**

Prof. Dr. Plewa
Dr. Baur

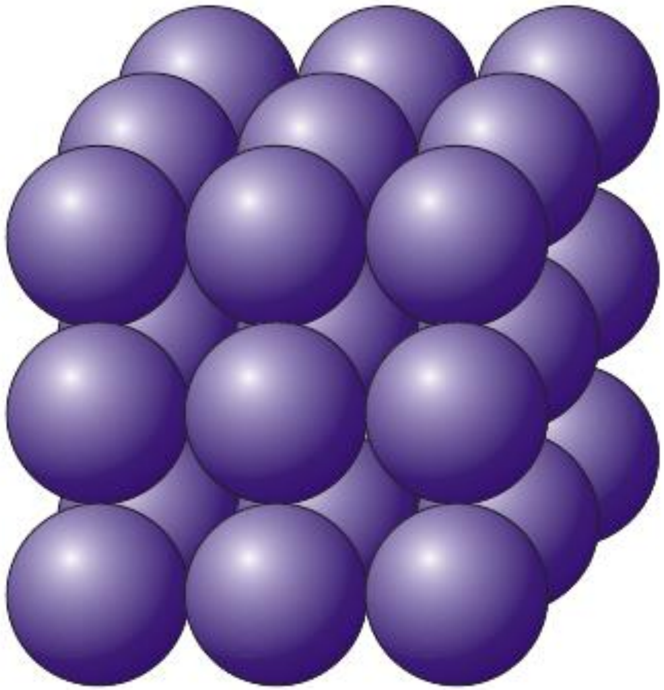
# Overview of Nano Materials

fraction of atoms at the surface as a function of particle diameter ($d_p$ = 0.5 nm).

| **Size (nm)** | **Number of atoms** | **Fraction at surface (%)** |
|---|---|---|
| 0.5 | 1 | |
| 1.0 | 8 | 100 |
| 2.0 | 64 | 99 |
| 5.0 | 1.000 | 50 |
| 10.0 | 8.000 | 25 |
| 20.0 | 64.000 | 12 |

# Overview of Nano Materials

## Surface atoms



A cube consisting of 27 atoms has

- 1 atom in the bulk
- 6 atoms at the faces
- 12 atoms at edges
- 8 atoms at corners

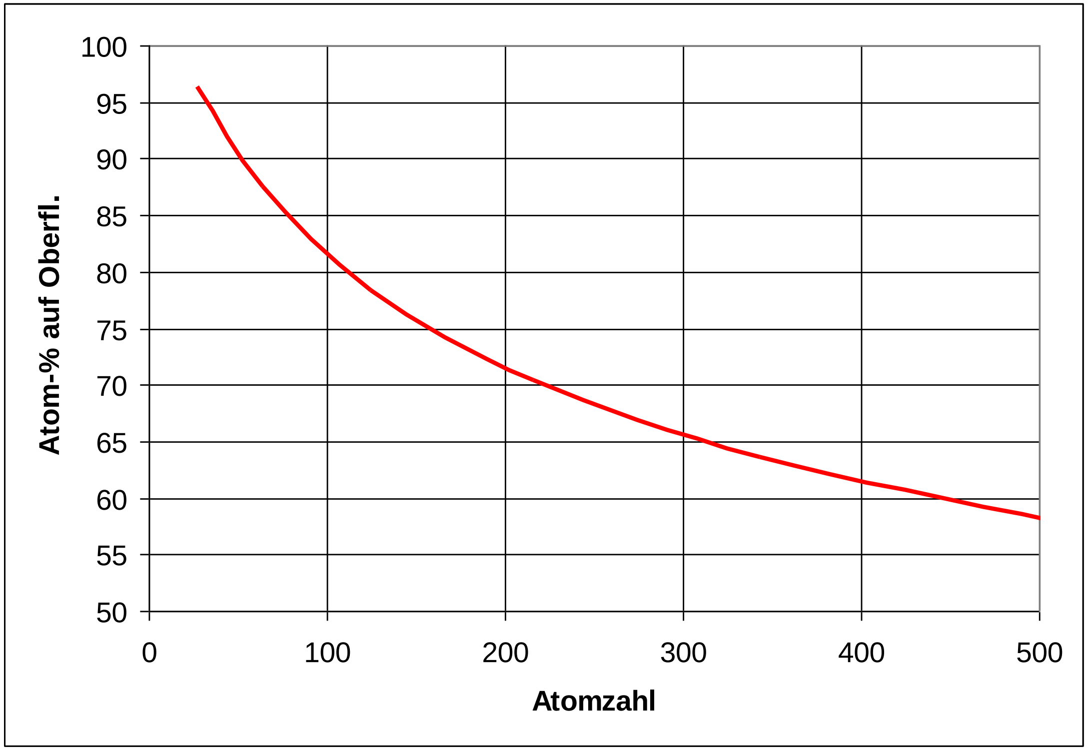
96% of atoms at surface

A cube consistsing of 64 atoms has
87.5% of atoms at surface

Prof. Dr. Plewa
Dr. Baur

# Overview of Nano Materials

## Surface atoms




n: length of cube

N: number of atoms ($N = n^3$)

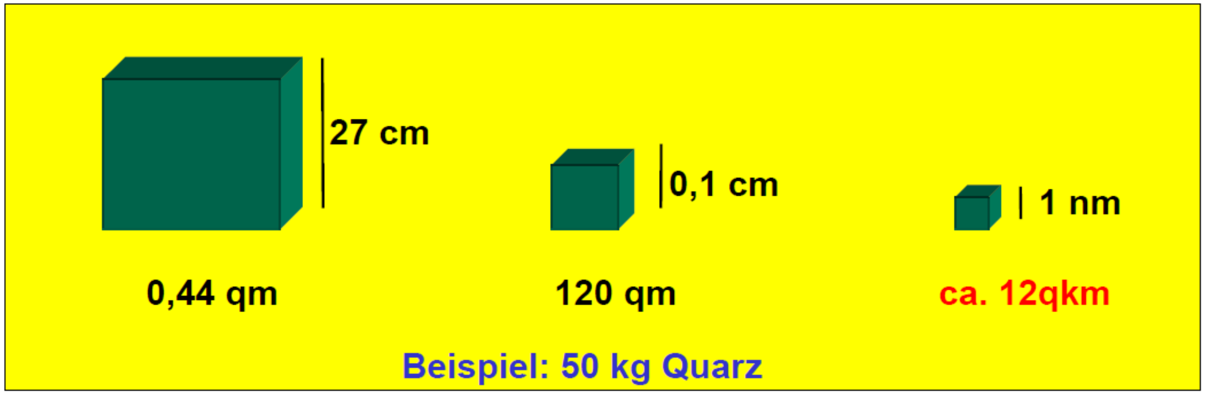
$N_0$: surface atoms

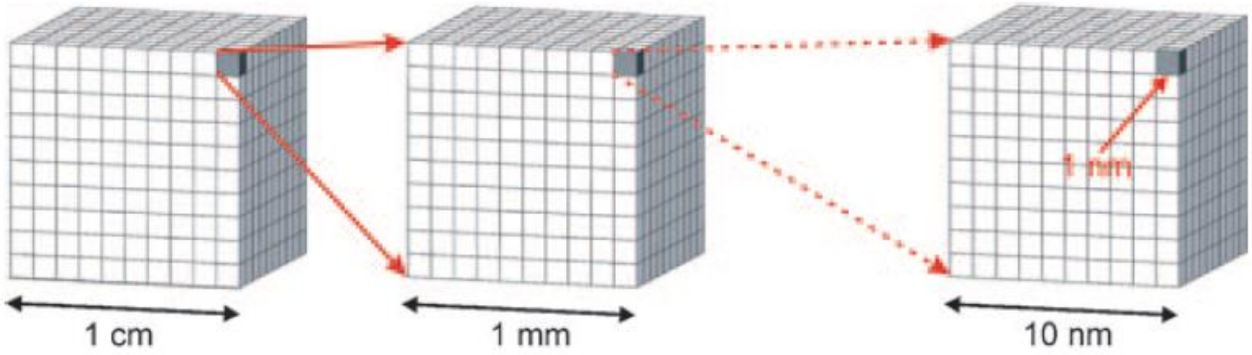
$N_0/N$: fraction of surface atoms

$$N_O = 8 + 6(n-2)^2 + 3(4n-8)$$

# Overview of Nano Materials

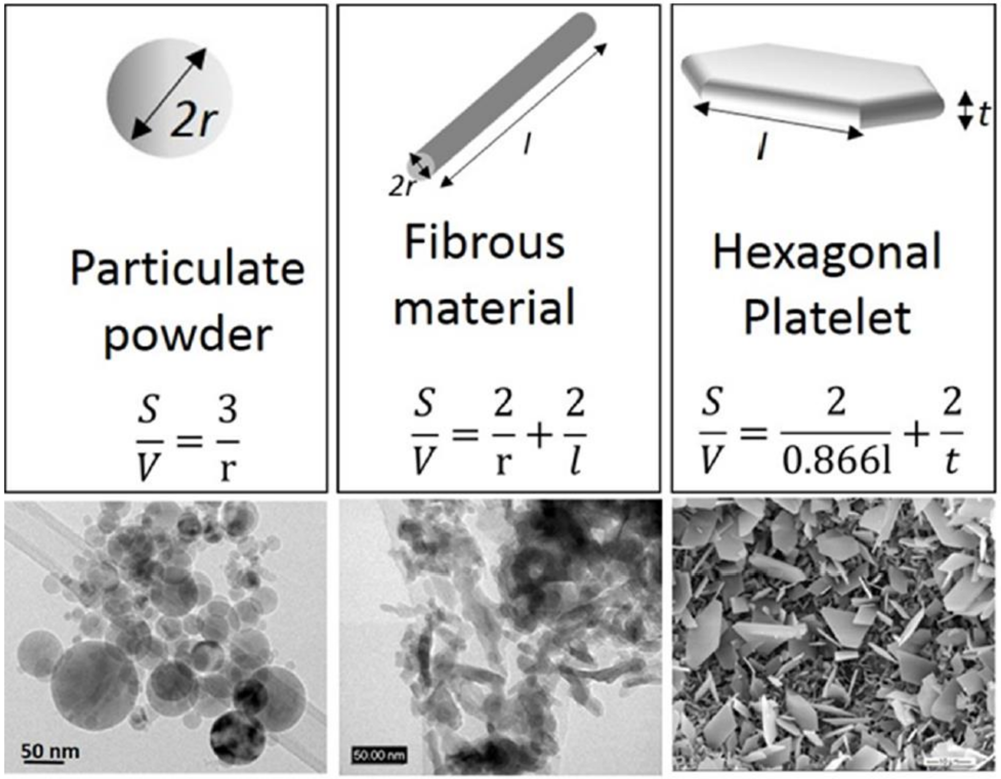
## Specific surface area




Prof. Dr. Plewa
Dr. Baur

# Overview of Nano Materials




Surface area/volume relations for different reinforcement geometries

Thostenson, E.T.; Li, C.; Chou, T.W.

# Overview of Nano Materials

## Specific surface area

$$\mathrm{SSA} = \frac{S_{\mathrm{total}}}{m_{\mathrm{total}}}$$

$$S_{\mathrm{part}} = \pi D^2 \qquad S_{\mathrm{total}} = n * S_{\mathrm{part}}$$

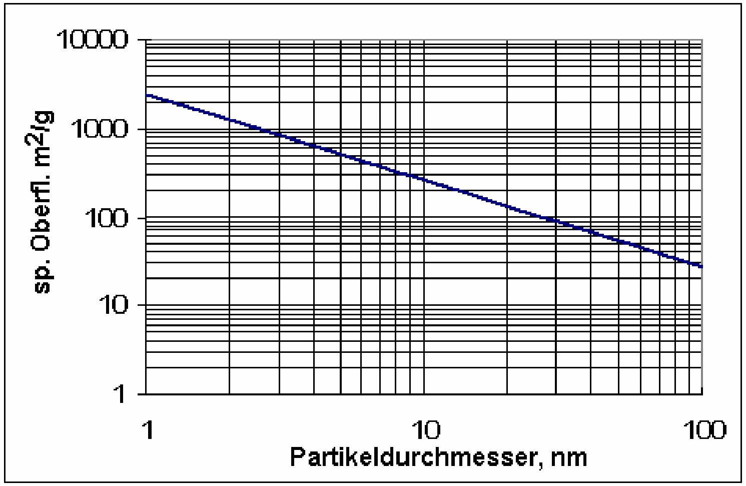
$$m_{\mathrm{total}} = V_{\mathrm{total}} * \rho$$

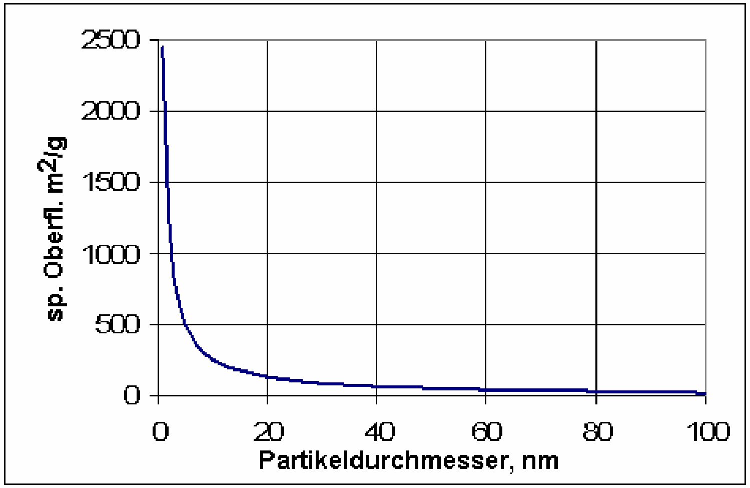
$$V_{\mathrm{part}} = \frac{4}{3}\pi\frac{D^3}{8} \qquad V_{\mathrm{total}} = n * V_{\mathrm{part}}$$

$$\mathrm{SSA} = \frac{n * \pi D^2 * 3 * 8}{n * \pi D^3 * 4 * \rho} = \frac{6}{D\rho}$$

$$[\mathrm{SSA}] = \frac{m^2 * m^3}{m^3 * kg} = \frac{m^2}{kg}$$

$$\boxed{SSA \sim \frac{1}{D}}$$



# Overview of Nano Materials

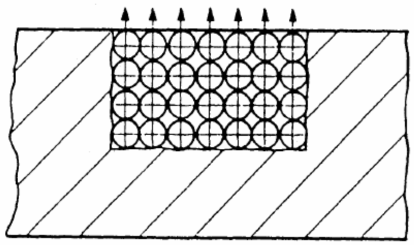
## Surface atoms

Verhältnis der Oberflächenatome zur Gesamtzahl der Atome von $\alpha$-$Al_2O_3$-Partikel und $ZrO_2$-Partikel

| Partikel-durchmesser [nm] | Anzahl der Oberflächenmoleküle [%] | | |
|---|---|---|---|
| | $\alpha$-$Al_2O_3$ | $ZrO_2$ (monoklin) | $ZrO_2$ (tetragonal) |
| 10 | 21,1 | 14,8 | 14,6 |
| 100 | 4,4 | 3,1 | 3,0 |
| 1.000 | 2,8 | 1,9 | 1,9 |

- Densely packed atoms result in a larger number of surface atoms

- Surface atoms bond to ubiquitous ions such as $OH^-$, $H_2O$ or $O^{2-}$



# Overview of Nano Materials

- **Surface atoms are in a higher energetic state**

- **this increases their suitability for absorption, heat exchange, sensing,…**

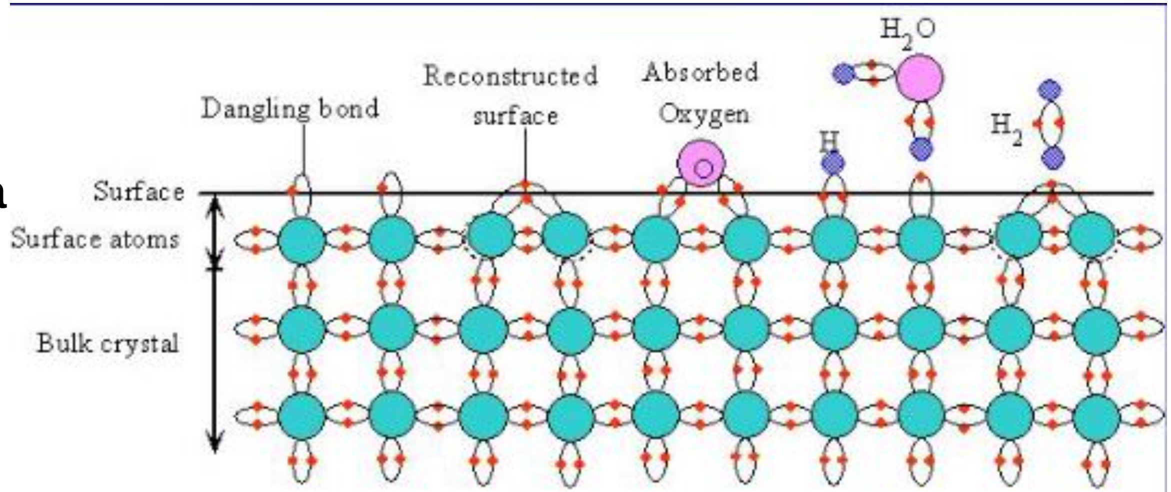



Fig. 1.52: At the surface of a hypothetical two dimensional crystal, the atoms cannot fulfill their bonding requirements and therefore have broken, or dangling, bonds. Some of the surface atoms bond with each other; the surface becomes reconstructed. The surface can have physisorbed and chemisorbed atoms.

From *Principles of Electronic Materials and Devices, Second Edition*, S.O. Kasap (© McGraw-Hill, 2002)
http://Materials.Usask.Ca

# Overview of Nano Materials

**Dependence of Material Properties on the Size of Nano Particles**

Prof. Dr. Plewa
Dr. Baur

# Overview of Nano Materials

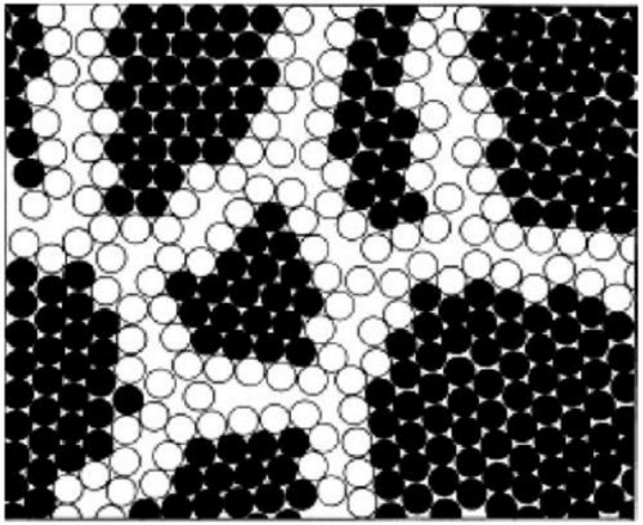
**Depending on the diameter, different properties are influenced:**

| | |
|---|---|
| Catalytic activity | < 5 nm |
| Magnets get „softer“ | < 20 nm |
| Refraction | < 50 nm |
| Electromagnetic phenomena (“supra paramagnetism”) | < 100 nm |
| Electric phenomena (“supra conduction”) | < 100 nm |
| Mechanical properties (increased hardness) | < 100 nm |

Kamigaito et al (*Jpn. Soc. Powder Metall*. 38 (1991) 315)

# Overview of Nano Materials

Nanocrystalline materials may exhibit increased strength/hardness, improved toughness, reduced elastic modulus and ductility, enhanced diffusivity, higher specific heat, enhanced thermal expansion coefficient (CTE), and superior soft magnetic properties in comparison with conventional polycrystalline materials.



statistisch orientierte Körnern (schwarz)

Two-dimensional model of a nanostructured material. The atoms in the centers of the crystals are indicated in black. The ones in the boundary core regions are represented as open circles

*M.A. Meyers et al. / Progress in Materials Science 51 (2006) 427–556*

Sizes:

| | |
|---|---|
| Atom | 0.001 nm |
| Nano granule | ~10 nm |
| Boundary | ~1 nm |
| Glide plane | 0.1 nm |

Prof. Dr. Plewa
Dr. Baur

# Overview of Nano Materials

The chemical, optical, electrical, and magnetic properties of n**ano particles** depend both on their size (1-10 nm) as well as their morphology (sphere, rod, leaves,…).

**Copper colloids** are catalitically active and are used to convert syngas to methanol

**Titanium** dioxide nano particles can be used in solar cells, for the photochemical wastewater detoxification, as a UV-absorber and so on…

**CdSe** nano particles, so-called quantum dots, are used as fluorescent markers for in vivo measurements or in displays

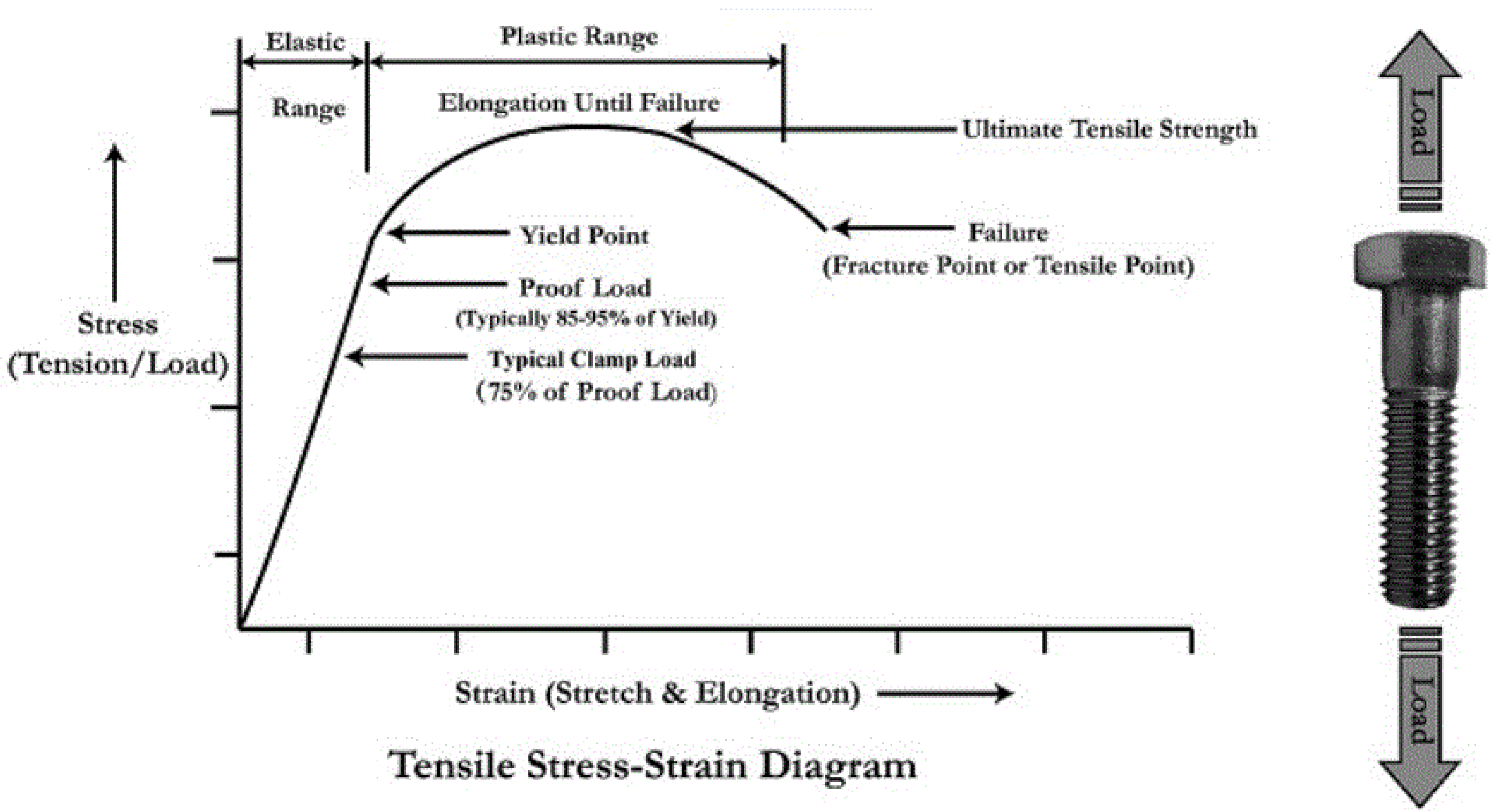
# Mechanical Properties

## Definitions

### Mechanical Properties

- Elasticity
  - non permanent deformation
- Plasticity - permanent deformation
- Strength - ability to withstand load
- Ductility - ability to be drawn into wire
- Malleability - ability to deform under compression
- Hardness -resistance to abrasion, wear, scratch, cut
- Brittleness - fracture without warning
- Toughness -amt of energy absorbed before rupture
- Stiffness - to resist deformation Al v/s steel beam (sag)
- Resilience - resist impact/ shock, absorb energy upto elastic limits
- Fatigue - under alternating stresses
- Creep - slow & progressive deform.. at const stress & at high temp

# Mechanical Properties





Prof. Dr. Plewa
Dr. Baur

# Mechanical Properties

Table 1-2.—Mechanical Properties of Metals/Alloys

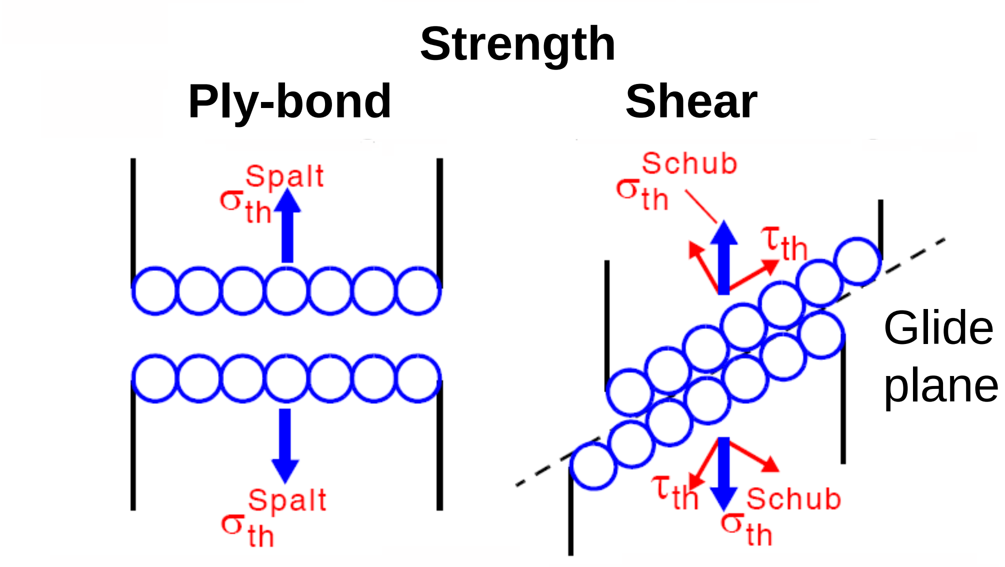
| TOUGHNESS | BRITTLENESS | DUCTILITY | MALLEABILITY | CORROSION RESISTANCE |
|---|---|---|---|---|
| Copper | White Cast Iron | Gold | Gold | Gold |
| Nickel | Gray Cast Iron | Silver | Silver | Platinum |
| Iron | Hardened Steel | Platinum | Aluminum | Silver |
| Magnesium | Bismuth | Iron | Copper | Mercury |
| Zinc | Manganese | Nickel | Tin | Copper |
| Aluminum | Bronzes | Copper | Lead | Lead |
| Lead | Aluminum | Aluminum | Zinc | Tin |
| Tin | Brass | Tungsten | Iron | Nickel |
| Cobalt | Structural Steels | Zinc | | Iron |
| Bismuth | Zinc | Tin | | Zinc |
| | Monel | Lead | | Magnesium |
| | Tin | | | Aluminum |
| | Copper | | | |
| | Iron | | | |

* Metals/alloys are ranked in descending order of having the property named in the column heading

**Examples of metals/alloys possessing certain mechanical properties**

# Mechanical Properties

Mechanical Properties of Materials




All chemical bonds are breaking

Two layers are moving
→ bonds are not broken

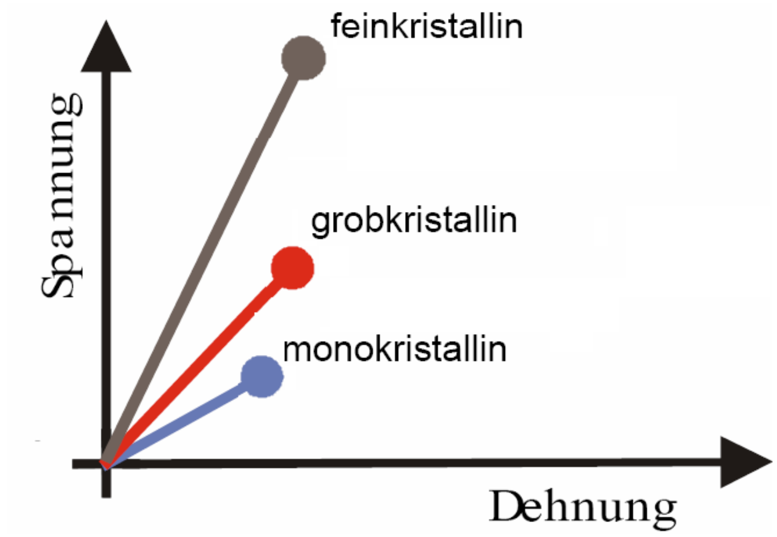
Prof. Dr. Plewa
Dr. Baur

# Mechanical Properties

Yield strength $R_e$ of nano materials

A decrease in grain diameter results in a significant increase in strength

The extraordinary combination of both high strength and high ductility




Large yield strength (highly elastic material)

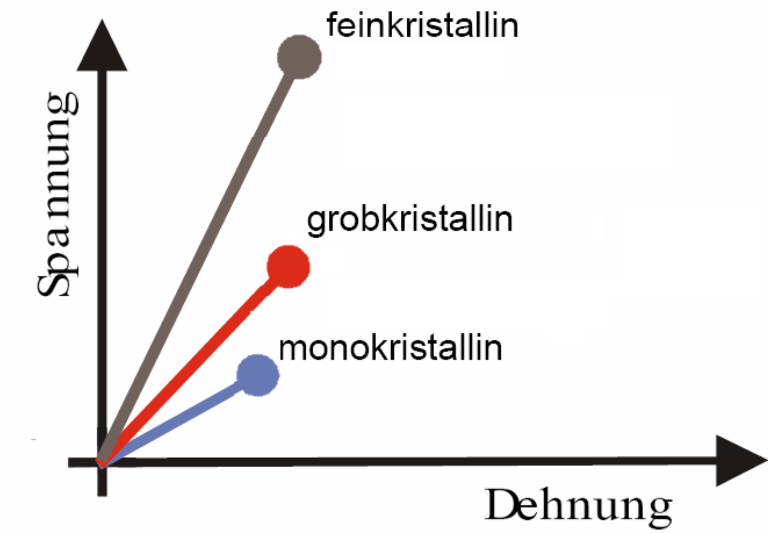
-Material (crystals) without dislocations

-Material with dislocations and barriers for their movement

Elasticity

Prof. Dr. Plewa
Dr. Baur

# Mechanical Properties



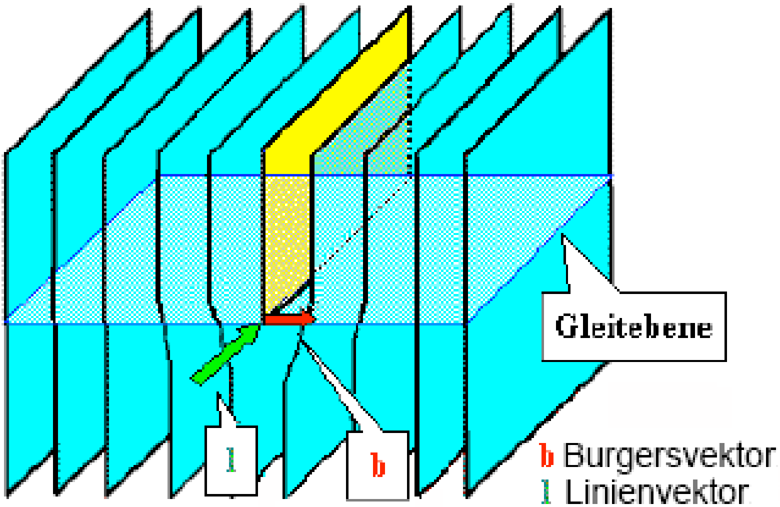

The extraordinary combination of both high strength and high ductility

*Normally, materials may be strong or ductile, but not at once.*

Nevertheless, some nanostructured materials retain its high strength and ductility under deformation.

The mechanisms of improving of ductility are an increase of grain boundary sliding and grain rotation

# Mechanical Properties




Mechanic stress above the yield strength causes parts of the material to glide relative to others.

These dislocations can only move until they reach a grain boundary.

Plastizität

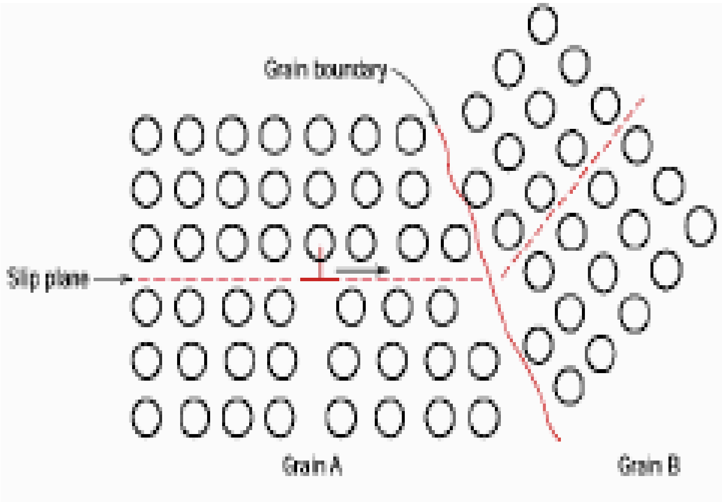
Prof. Dr. Plewa
Dr. Baur

# Mechanical Properties

Mechanical properties of materials

Dislocations can only move until they reach a grain boundary.

The boundaries present a barrier that cannot be passed by the dislocation. A so-called „dislocation pile-up“ occurs.




Hall-Petch relation:

$\tau_{gb} \approx k_y * D^{-1/2}$

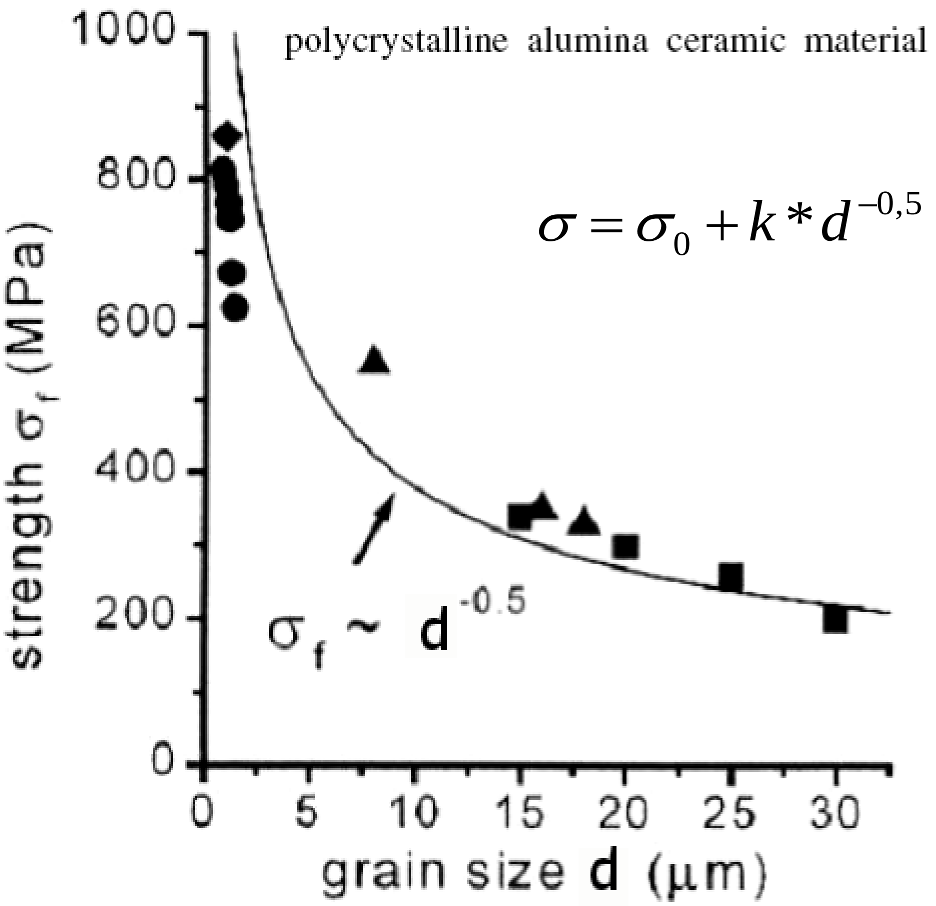
Small grain diameters D result in smaller additional stress $\tau_{gb}$

The dislocation pile-up causes a high resistance towards deformation – **hardness and strength increase**

Plastizität


Prof. Dr. Plewa
Dr. Baur

# Mechanische Eigenschaften von Nanomaterialien



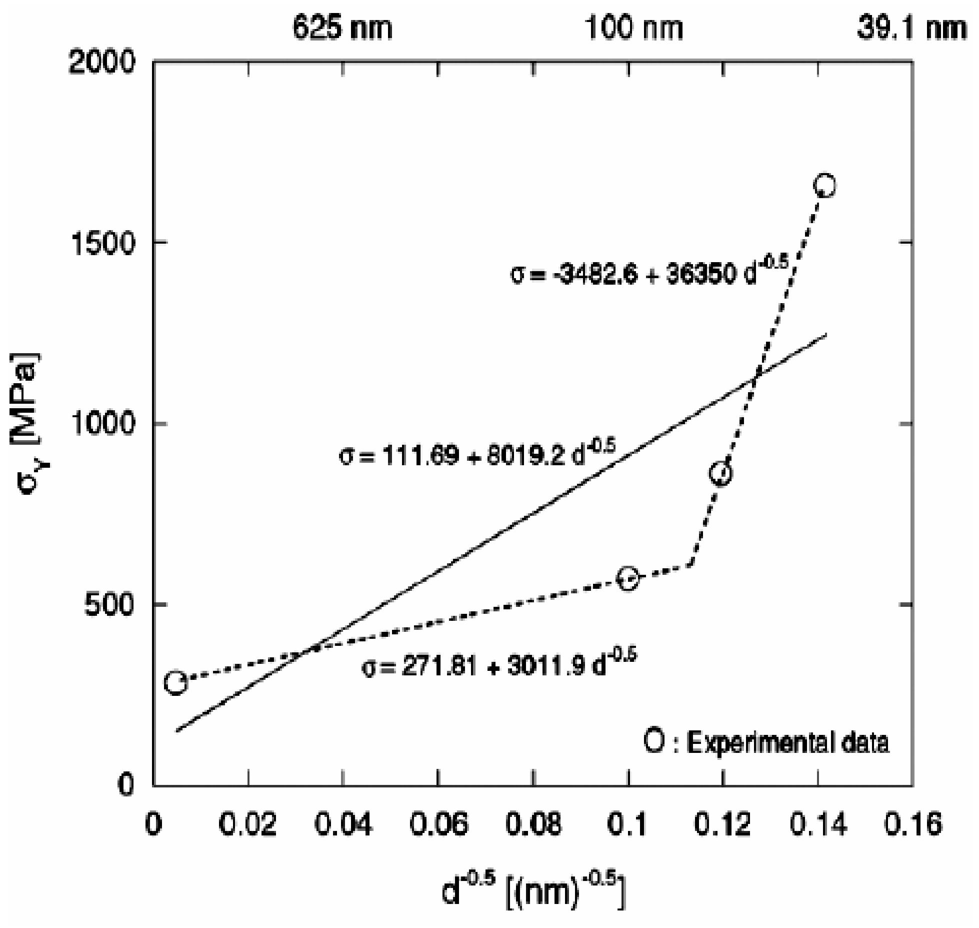

Relationship between grain size and mechanical strength for PCA.

(Theo G M M Kappen)

Prof. Dr. Plewa
Dr. Baur

# Mechanical Properties

Festigkeit von nanokristallinem Eisen in Abhängigkeit von der Korngröße



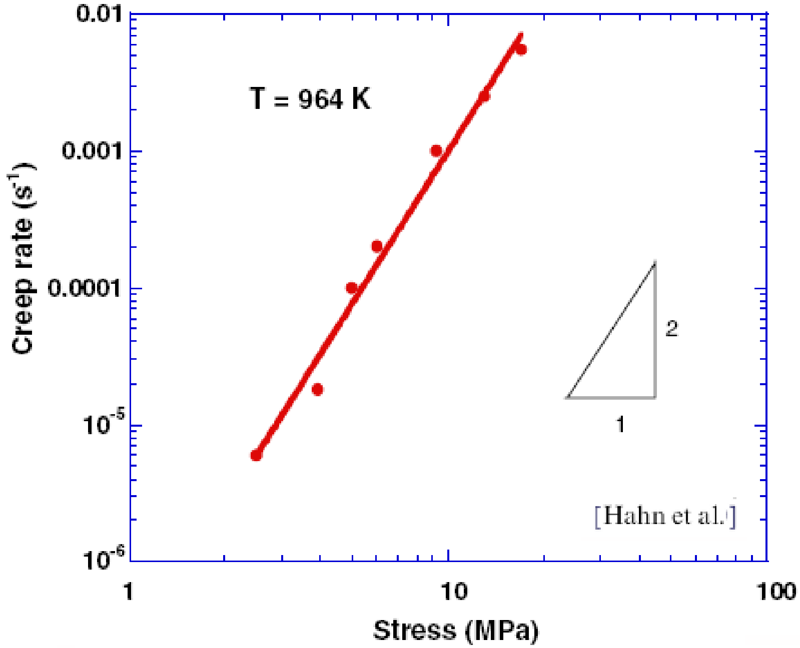

$$\sigma = \sigma_0 + k * d^{-0,5}$$

DVS

Prof. Dr. Plewa
Dr. Baur

# Mechanical Properties

creep of nanocrystalline materials




Stress versus strain rate plots for nanocrystalline $TiO_2$

grain-boundary diffusion is the operating mechanism in nanocrystalline creep

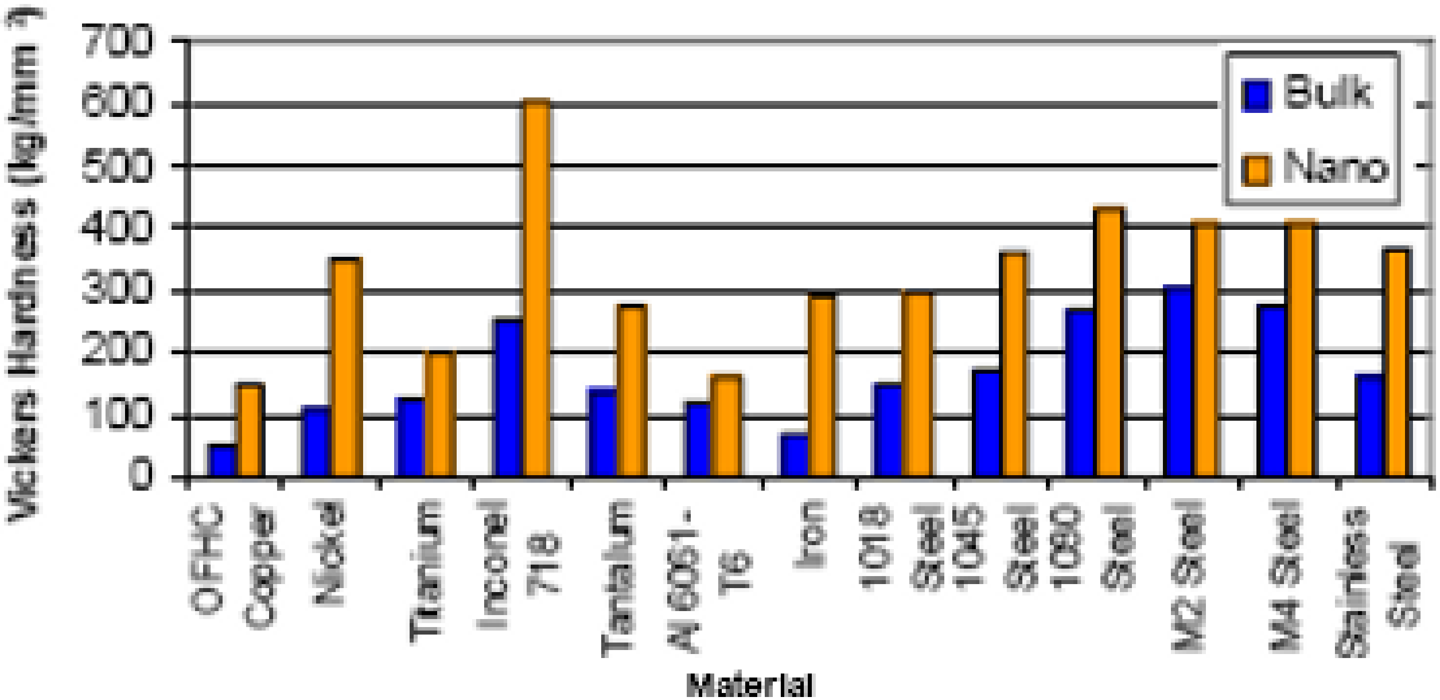
Nano crystalline $TiO_2$ (rutile) can be deformed plastically at temperatures between 600 and 800 °C.

Micro crystalline $TiO_2$ shows this creeping only at significantly higher temperatures close to the meltin point (1830 °C).

This has been attributed to diffusion along grain boundaries.

Prof. Dr. Plewa
Dr. Baur

# Mechanical Properties



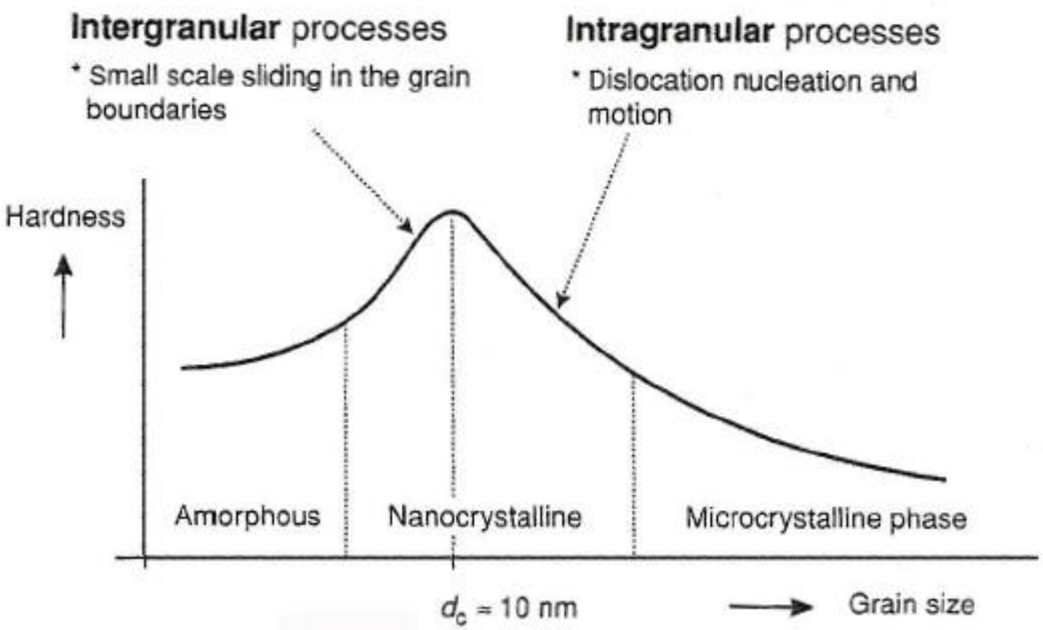

Nanostructured chips are typically 2-3 times as hard as bulk material

Kevin Trumble

In metallic nano materials hardness increases with decreasing ductability.

Prof. Dr. Plewa
Dr. Baur

# Mechanical Properties




Schematic illustration of development of the hardness in materials with decreasing grain size *d*.

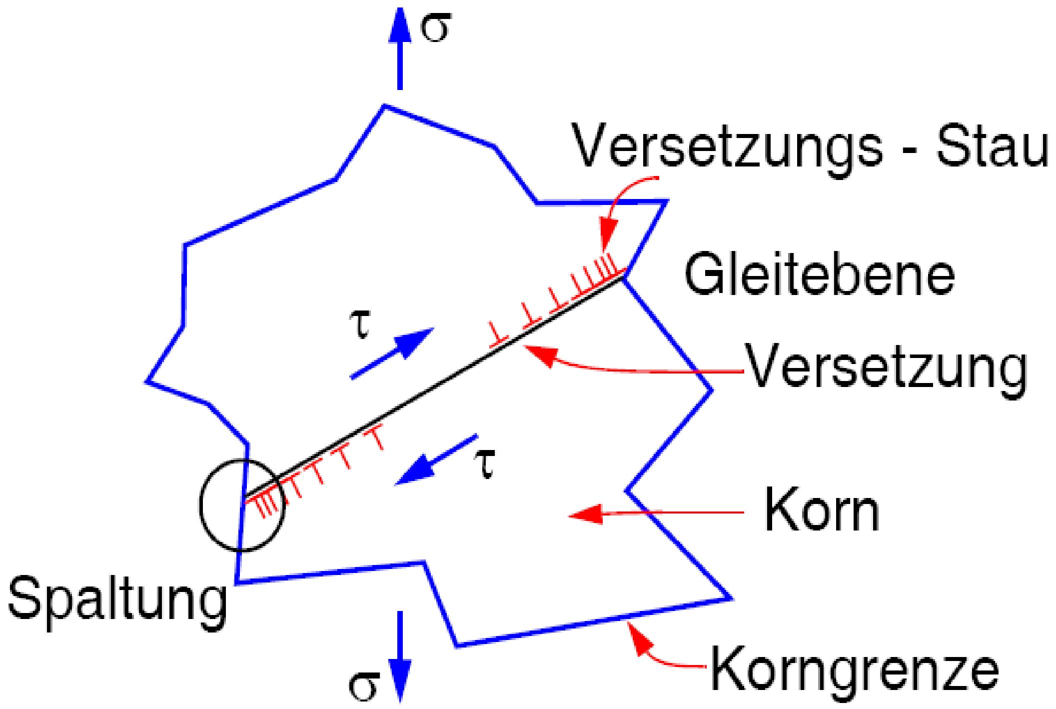
Room temperature hardness and elastic modulus values for nano-crystalline YSZ obtained from nanoindentation studies.

| Grain size (nm) | Hardness (GPa) | Modulus (GPa) |
|---|---|---|
| 12 | 5.8±0.5 | 145±20 |
| 15 | 6.5 | 170 |
| 20 | 6.7 | 150 |
| 40 | 6.8 | 180 |
| 100 | 5.7 | 130 |
| bulk (literature) | 12–17 | 200–220 |

Soyez *et al.* Appl. Phys. Lett., 77, 2000,1155

# Mechanical Properties

Ductility is caused by easy movement of dislocations along the glide planes



# Mechanical Properties

## Summary

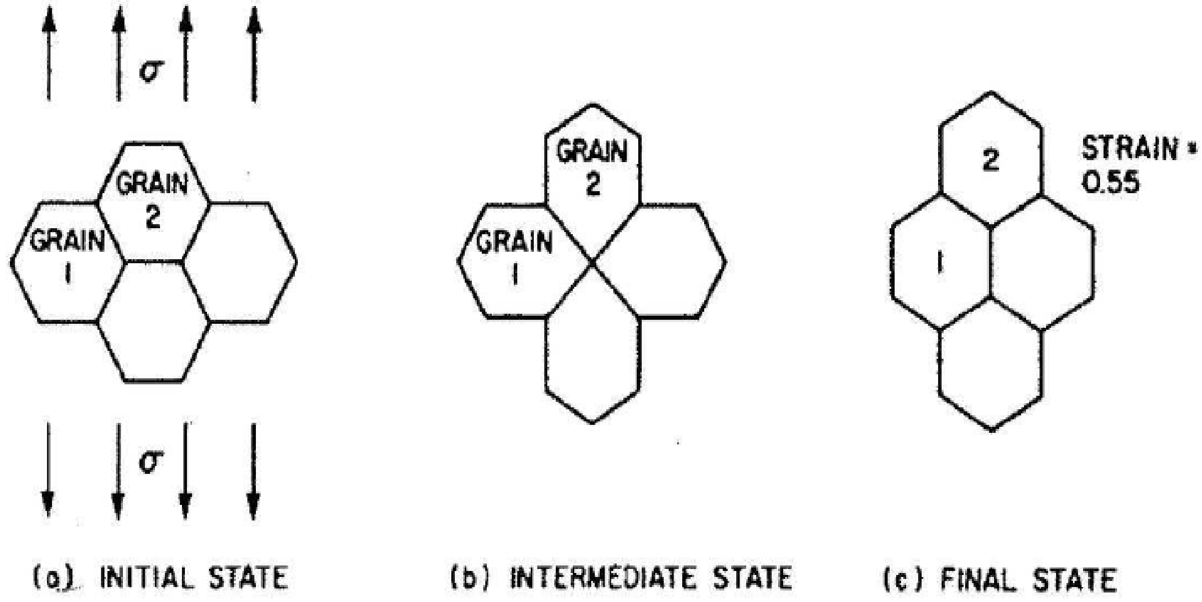
| Deformation | | |
|---|---|---|
| **elastic**<br>reversible deformation | **plastic**<br>irreversible deformation | **super plasticity**<br>irreversible deformation |
| Distortion of the lattice | Gliding of layers | Gliding of layers |
| Movement of atoms | Movement of dislocations | Movement of grain boundaries, dislocations and diffusion |

Atomic bonds are not broken

Atomic bonds are broken locally

# Mechanical Properties

## Mechanism of superplasticity




Grain boundary sliding is an important mechanism for high temperature creep of nanomaterials (grain swiching model)

Prof. Dr. Plewa
Dr. Baur

# Overview of Nano Ceramics

Most metallic materials are ductile and have high toughness.

Most ceramic materials have a high hardness and brittleness.

Nano sized materials (<20 nm) of the same chemical composition:

- Metals: high hardness and brittleness
- Ceramics: high ductility and high toughness

- Ductility - ability to be drawn into wire
- Malleability - ability to deform under compression
- Hardness -resistance to abrasion, wear, scratch, cut
- Brittleness - fracture without warning
- Toughness -amt of energy absorbed before rupture

Prof. Dr. Plewa
Dr. Baur

# Overview of Nano Ceramics

## Electrical properties

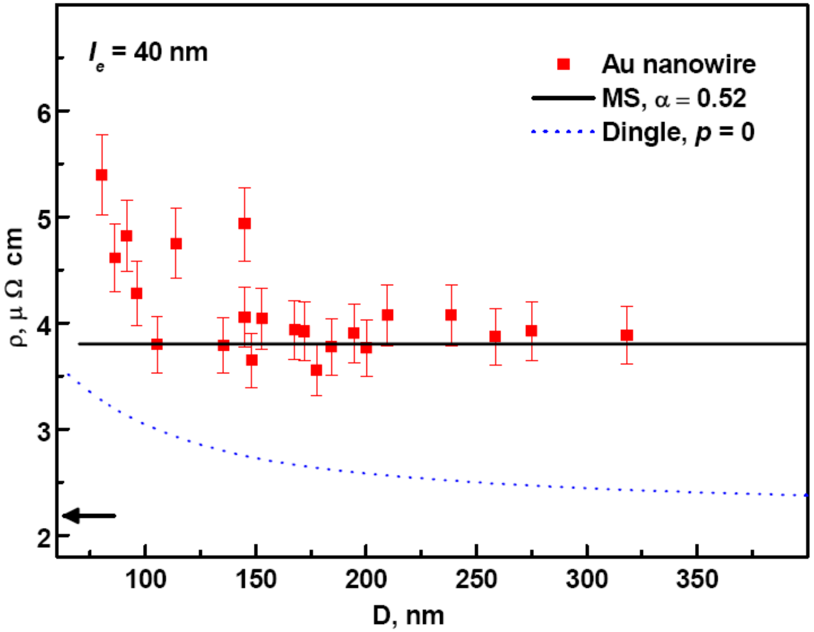
A result of the large specific surface area of nano particles:

- electrical resistance is large compared to macriocrystalline materials

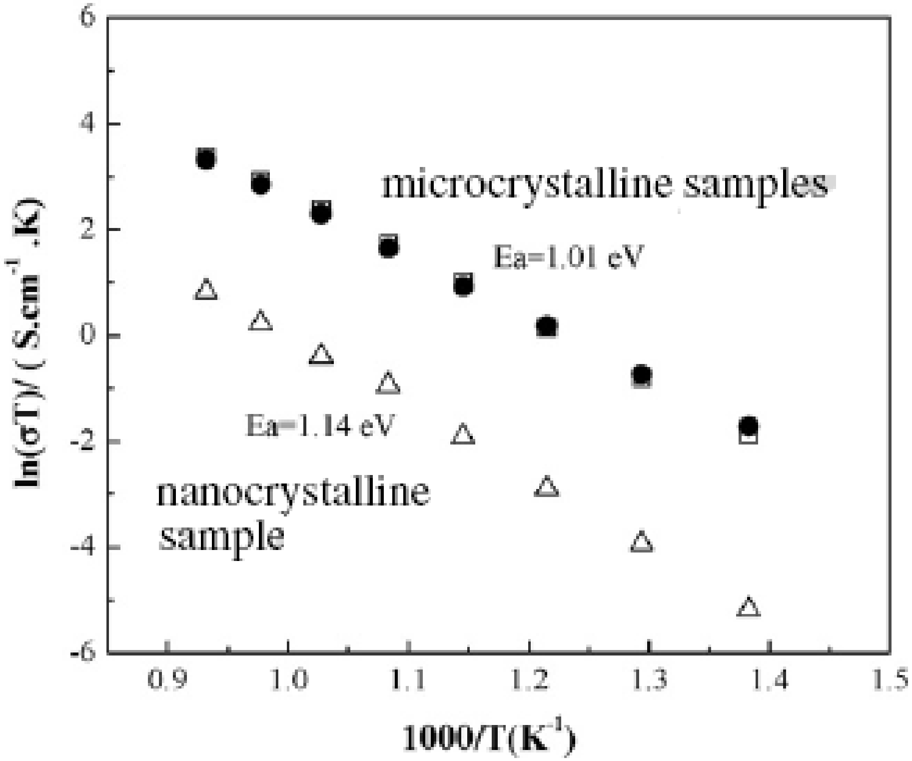
At diameters > 100 nm:

Electrons are mainly scattered at grain boundaries (number of grains is higher in nano ceramics)

At diameters < 100 nm additional electron scattering occurs at the surface of the wire. Resistance increases strongly.



# Electrical Properties




Arrhenius plots of electrical conductivities of 8YSZ: *Q. Li et al.*

Ion conductivity decreases with decreasing particle size.

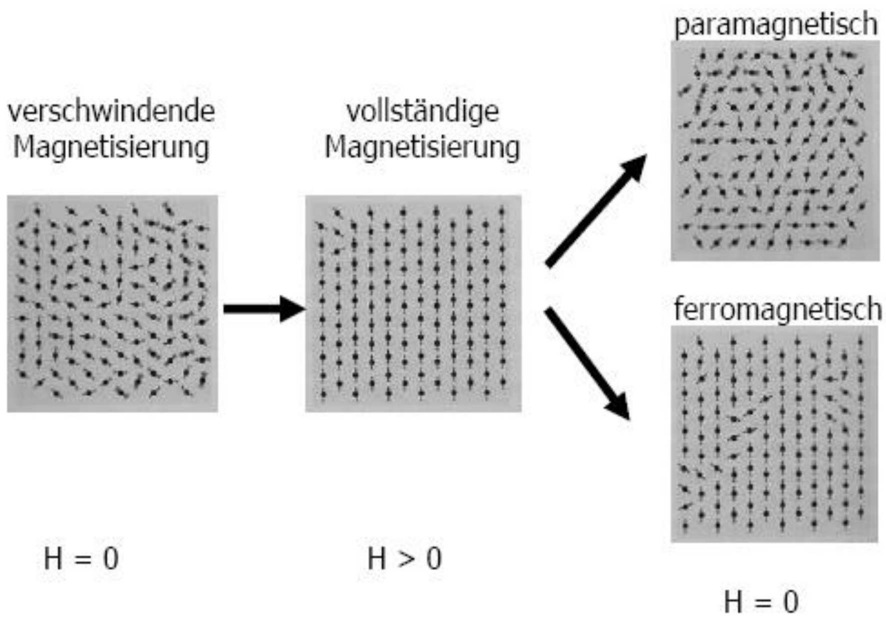
Grain boundaries begin to play a large role:

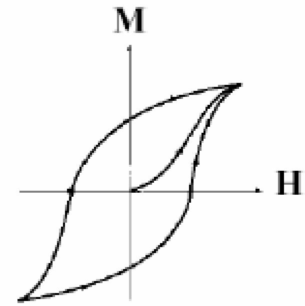
- Transition from bulk-controlled ionic conductivity to GB-controlled ionic conductivity
- Diffusion processes in the boundary layer are dominating

the absolute value of electrical conductivity for the nanocrystalline sample was one order of magnitude lower as compared to the microcrystalline samples,

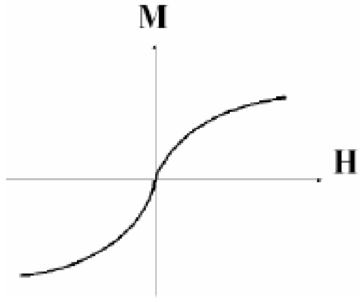
The nanocrystalline sample has a higher density than the microcrystalline samples , and high density should improve the electrical conductivity to some extent.

# Magnetic Properties




Hystereseverhalten des Feldes H zur Magnetisierung M eines Ferromagneten



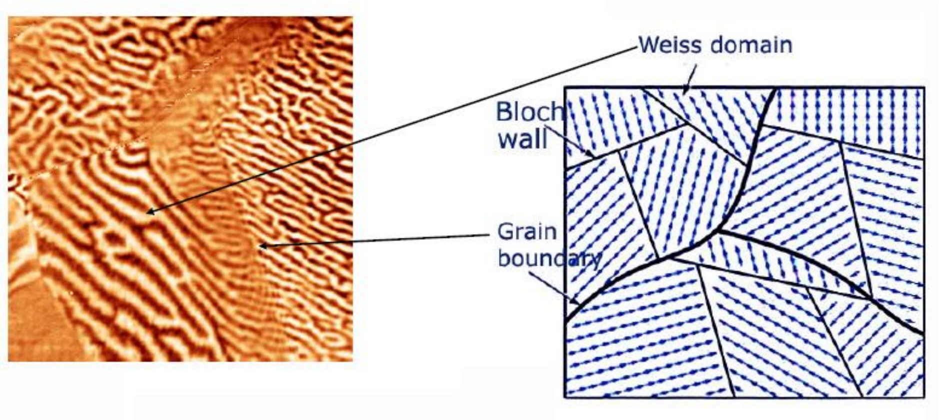

Para- und Superparamagneten zeigen (fast) keine Hysterese

Prof. Dr. Plewa
Dr. Baur

# Magnetic Properties

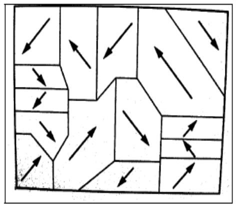
Area with identical magnetisation are called magnetic domains or Weiss domain.

The boundary is called Bloch wall.




A ferromagnetic material will have a magnetic moment even without an external magnetic field.

Interaction between electron spins favours parallel ordering.



At temperatures above the Curie temperature this ordering will be destroyed and the magnetic moment is lost.

# Magnetic Properties

Diameter of magnetic domains: 10-100nm

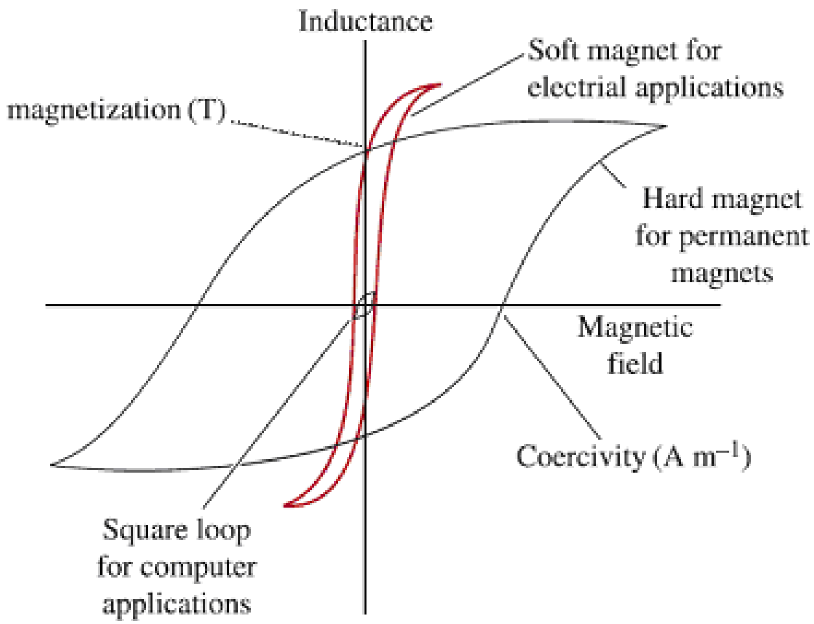
→ Nano particles consist of a single magnetic domain!

→ Upon polarity reversal the whole particle will be affected

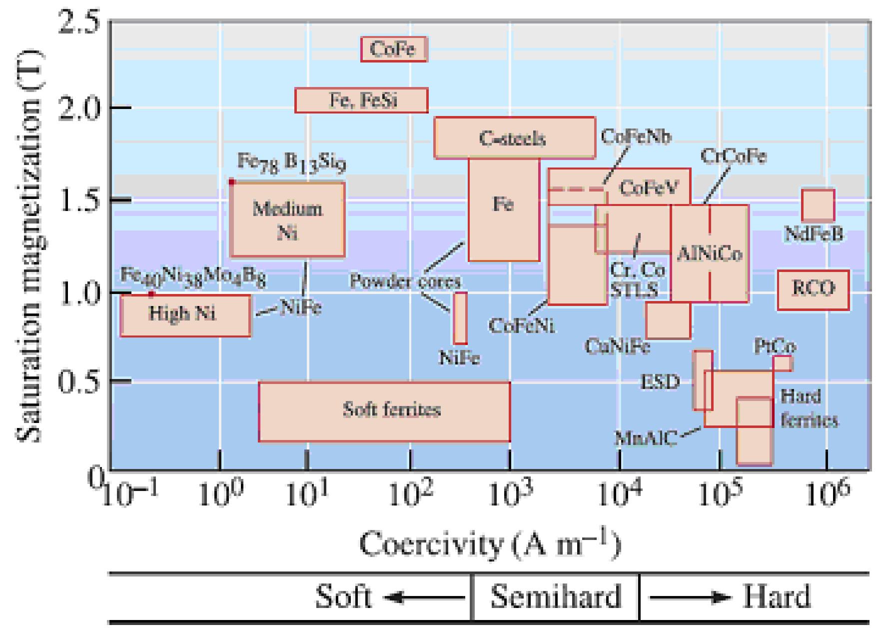
This requires significantly less energy as no interaction between magnetic domains occurs:

→ Hysteresis is much less pronounced

# Magnetic Properties




(a)




(b)

(a) Comparison of the hysteresis loops for three applications of ferromagnetic and ferrimagnetic materials.

(b) Saturation magnetization and coercivity values for different magnetic materials. (*by G.Y. Chin et al.*)

# Magnetic Properties

**Single-domain ferromagnetic particles**

The critical radius $r_c$ below which a particle acts as a single domain particle is given by

$$r_c \approx 9\frac{(AK_u)^{1/2}}{\mu_0 M_s^2}$$

where $\boldsymbol{A}$ is the exchange constant, $\boldsymbol{K_u}$ is the uniaxial anisotropy constant, $\boldsymbol{\mu_0}$ is called constant of permeability, and $\boldsymbol{M_s}$ is the saturation magnetization.

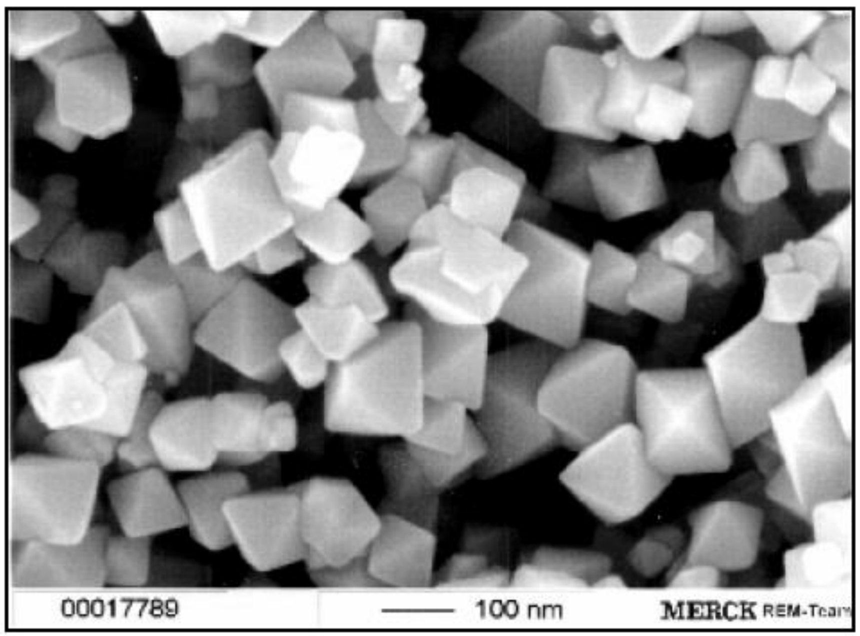
Typical values for $\boldsymbol{r_c}$ are about 15 nm for Fe and 35 nm for Co, for $\gamma$-$Fe_2O_3$ it is 30 nm, while for $SmCo_5$ it is as large as 750 nm

# Magnetic Properties

## Single domain nano particles

Critical radii ($r_c$):

Fe – 15 nm, Co – 35 nm, $Fe_2O_3$ - 30 nm, $SmCo_5$ – 750 nm




$Fe_2O_3$ Nanoteilchen (Magnetit)

# Magnetic Properties

## Single domain particles:

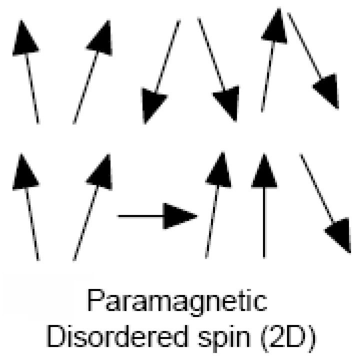
- **weak magnetic fields are sufficient to fully magnetize the material (low interaction of domains)**
- **removal of the field results in loss of magnetisation**
- **decreasing the particle size increases the softness of the magnet**

→ **„super parmagnetism“**

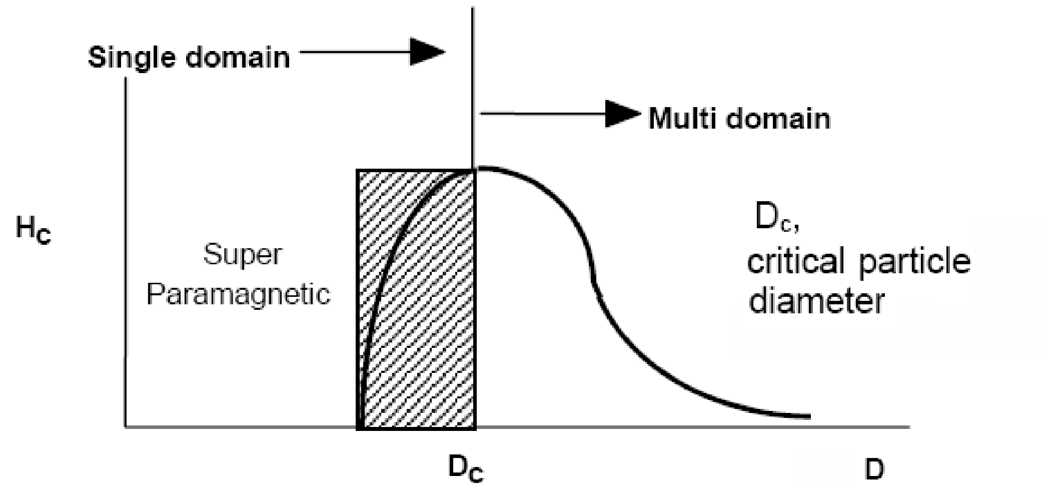
Paramagnets show hardly any hysteresis even as macro particles!

# Magnetic Properties

## Super-paramagnetism



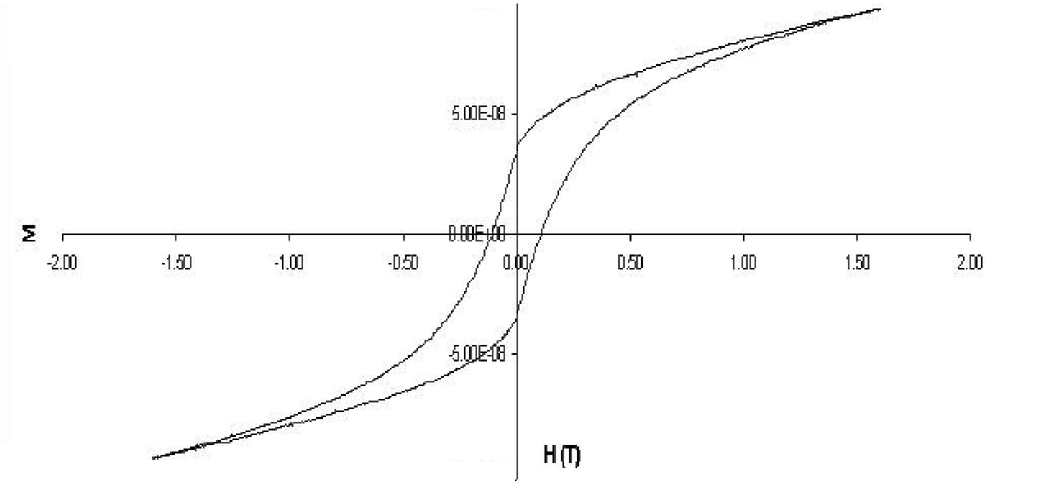

spin-coupling behaviours



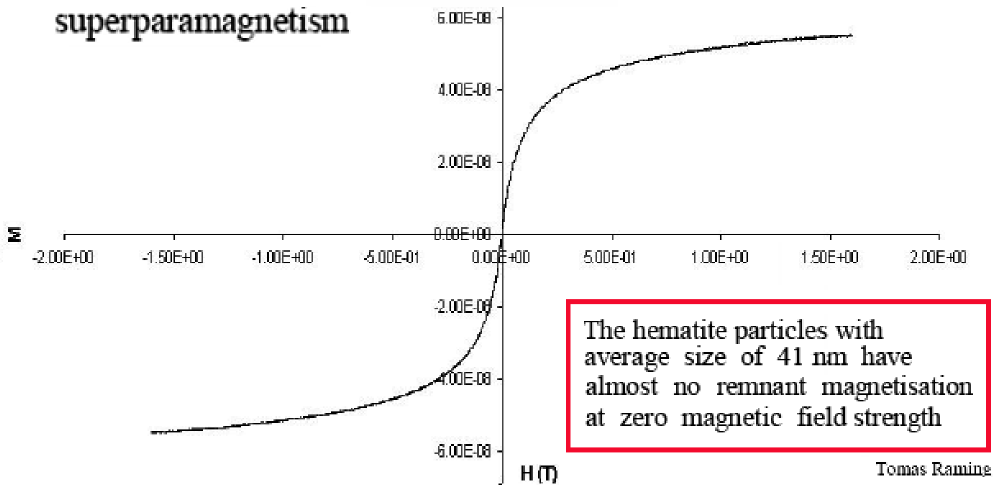

Qualitative illustration of the behaviour of the coercivity in ultrafine particle systems are the particles size changes.

*J. Dutta & H. Hofmann:*

# Magnetic Properties




Magnetisation measurement of subrounded hematite particles with 160 nm average size




Magnetisation measurement of subrounded hematite particles with 41 nm average size

Super paramagnetism

→ mainly a result of single domain particles

A ferromagnetic materials begins to behave like a paramagnetic material

Prof. Dr. Plewa
Dr. Baur

# Optical Properties

© Thomas Seilnacht

*Colour and particle size of gold nanoparticles*

| Shape | Size/nm | Colour |
|---|---|---|
| Spherical | <3 | Pale blue |
| | 12 | Pink |
| | 16 | Orange |
| | 20-40 | Red |
| | 70 | Dark magenta |
| | 100-150 | Violet |
| Irregular | 200 | Light Blue |
| Ellipsoids | 60x90 | Purple |
| Aggregated | | Blue |

The colour of the gold image depends on the dimensions of the nanoparticles, which are controlled by the parameters of the photochemical process.

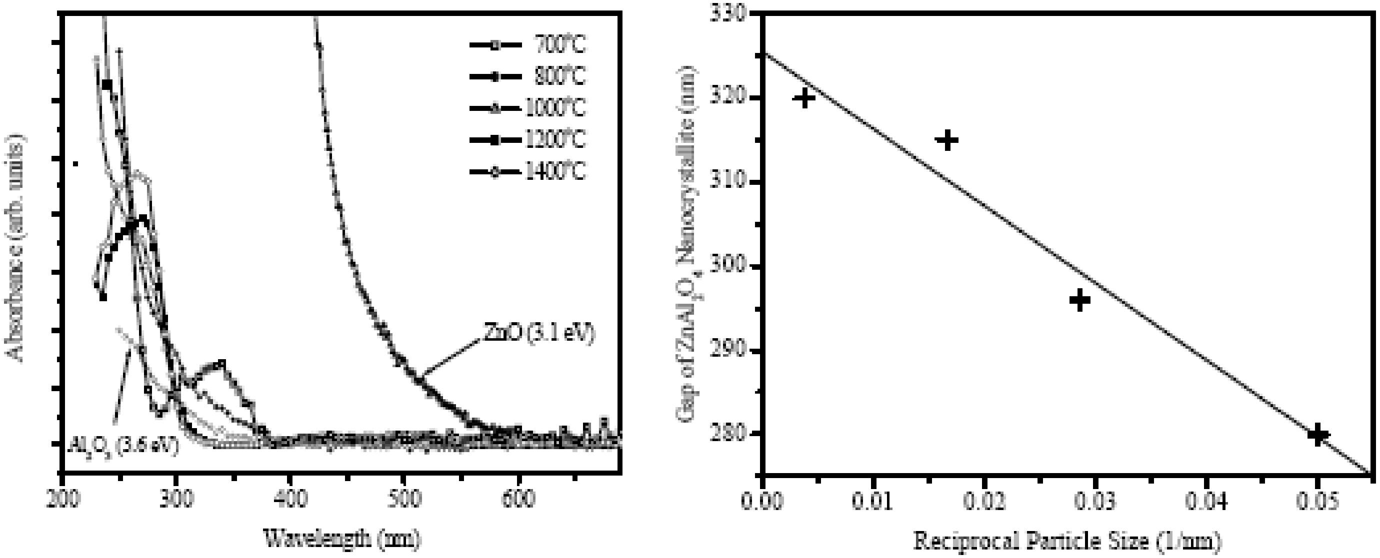
Mike Ware


Prof. Dr. Plewa
Dr. Baur

# Optical Properties

The band gap of a material increases with decreasing particle size:

→ instead of bands discrete energy levels are observed

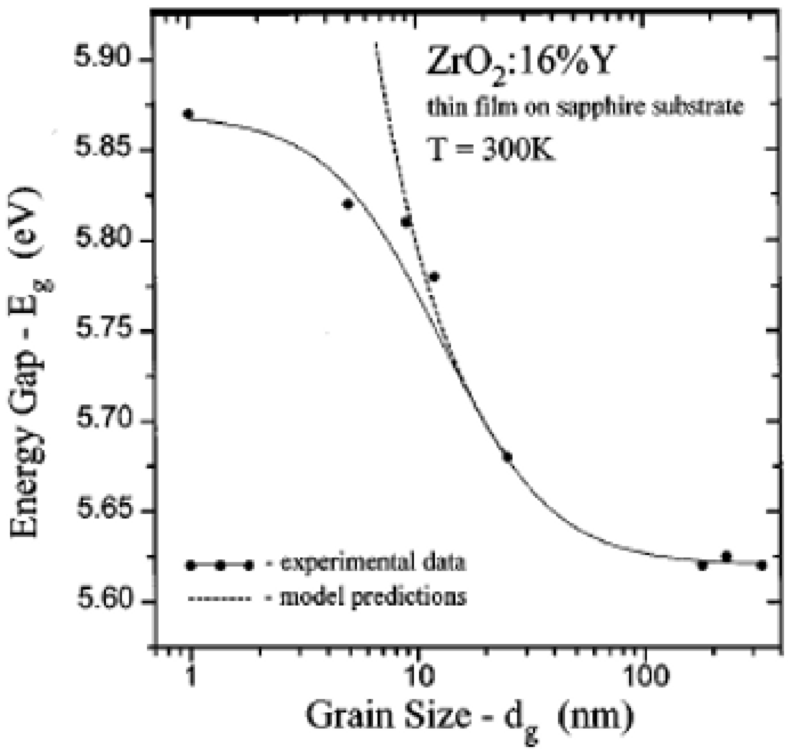



(a) Absorbance spectra of nanocrystalline $ZnAl_2O_4$ samples

(b) relationship between $ZnAl_2O_4$ bandgap and the particle size.

S. MATHUR

# Optical Properties




The band gap energy of $ZrO_2$:16%Y thin films as the function of their microstructure.

Kosacki, Petrovsky, and Anderson
Appl. Phys. Lett., 74, 1999, 341

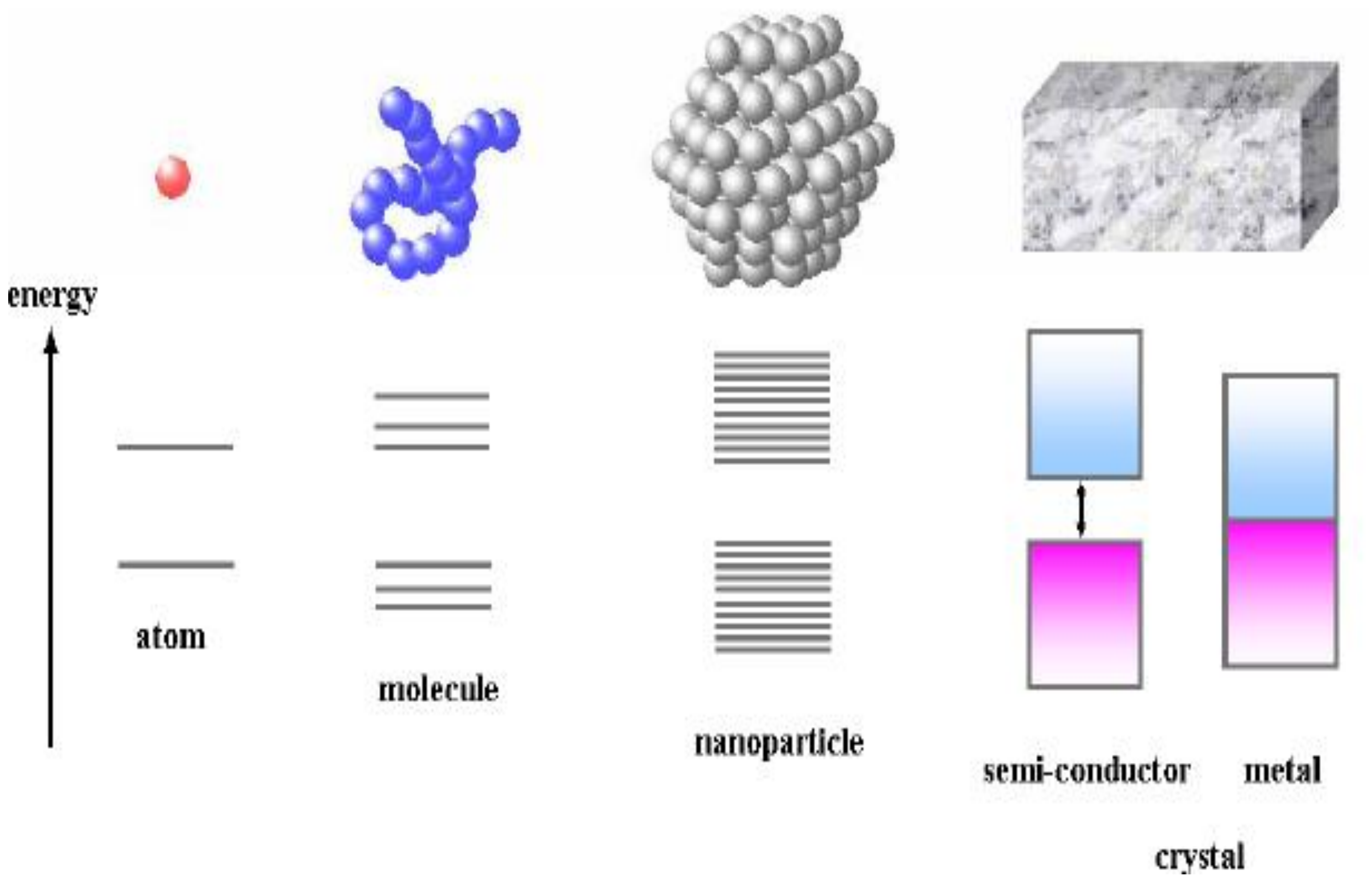
Band gap increases with decreasing particle size:

As can be seen, the energy gap changes little for specimens with the grain size larger than 100 nm, but rapidly increases when grain size decreases below 30 nm.

This change in the band gap can be utilized to tailor the emission wavelength of a particle.


Prof. Dr. Plewa
Dr. Baur

# Optical Properties

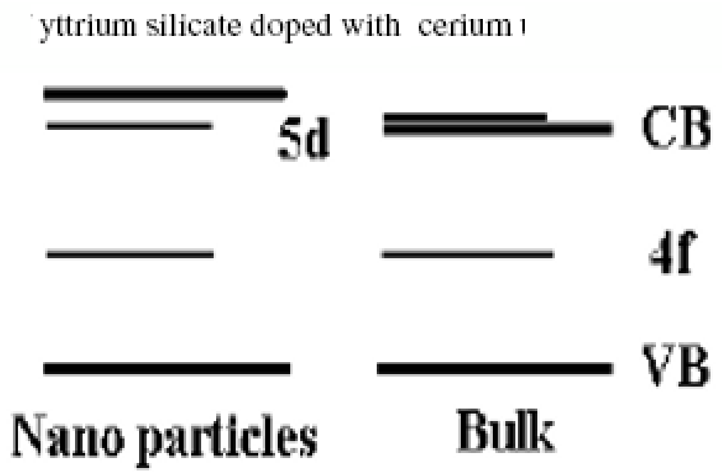




Prof. Dr. Plewa
Dr. Baur

# Optical Properties

Change of the band gap in $Y_2SiO_5:Ce^{3+}$

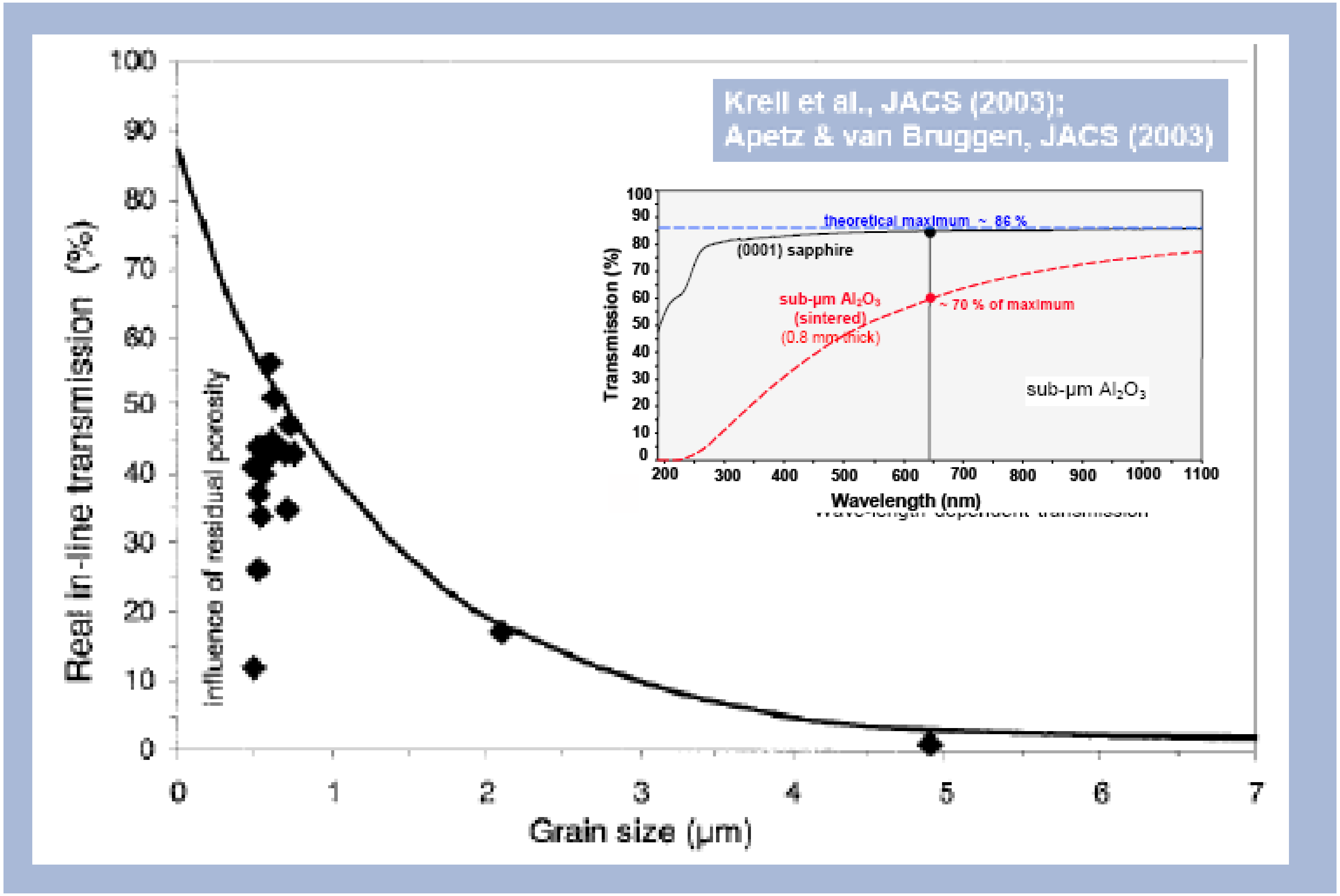



Energy band diagram showing the change in energy structure of cerium doped yttrium silicate leading to more efficient PL transition.

N Karar and H Chander

For example, the band gap of CdS was found to increase from 2.5 eV, the bulk value, to >3.5 eV as the particle diameter was decreased from 10nm to 1nm

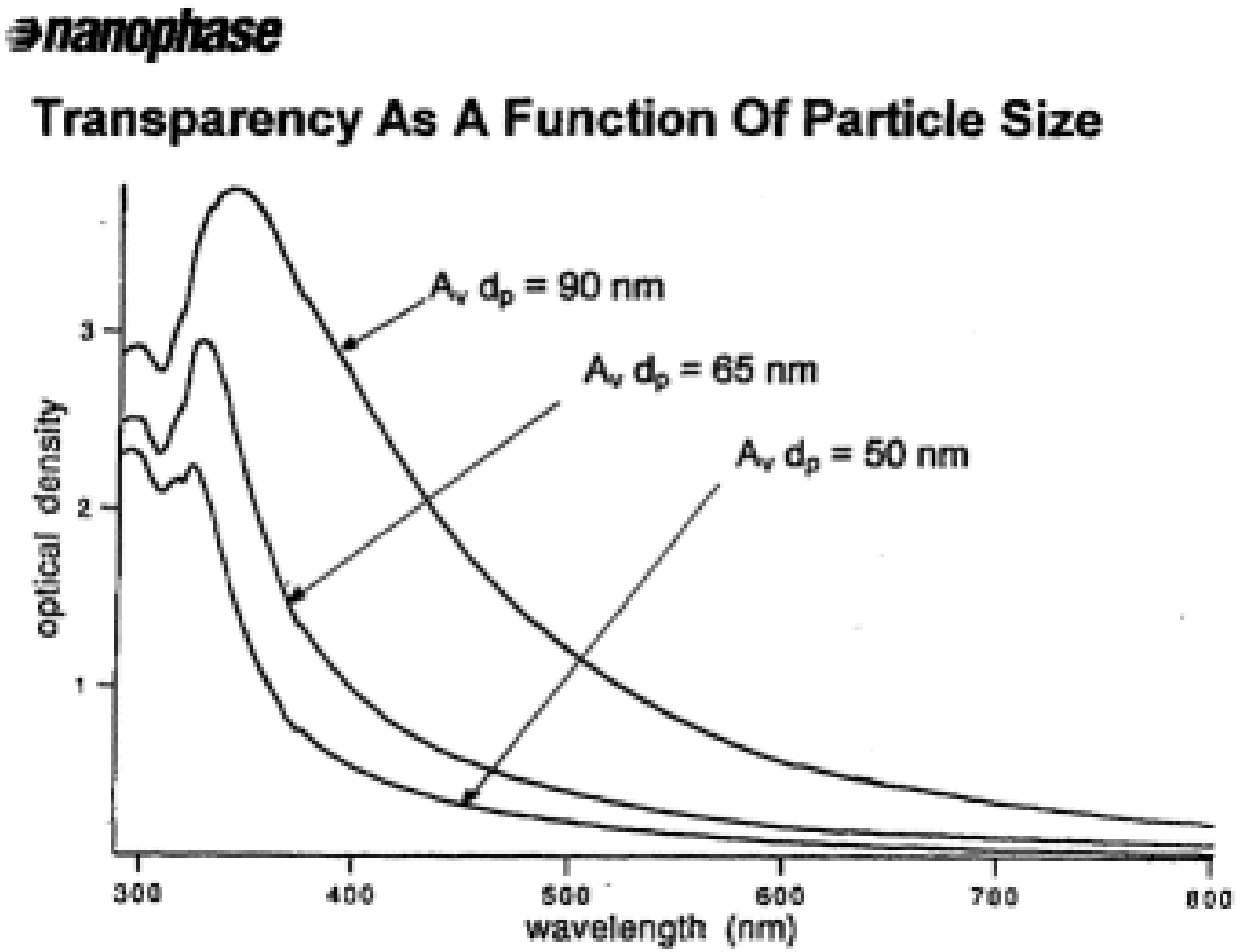
# Optical Properties




Transmission as a function of grain size

Prof. Dr. Plewa
Dr. Baur

# Optical Properties




**Extinction** or **optical density**

$$E = \log \frac{I_0}{I}$$

Transmission as a function of grain size

# Optical Properties

The color of a material depends on the size of the band gap

Nano scale particles show narrow absorption and scattering

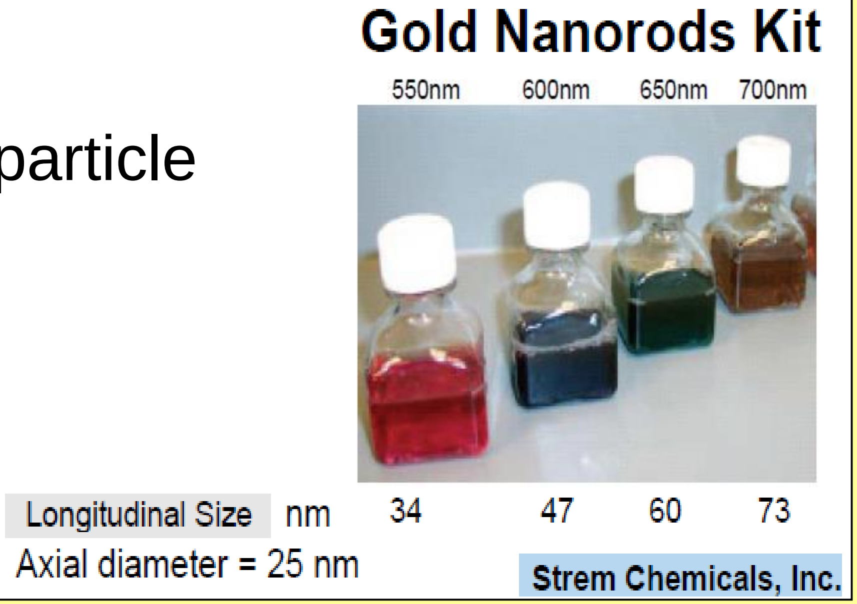
Color depends on:

-particle morphology

-interaction between particle

-…

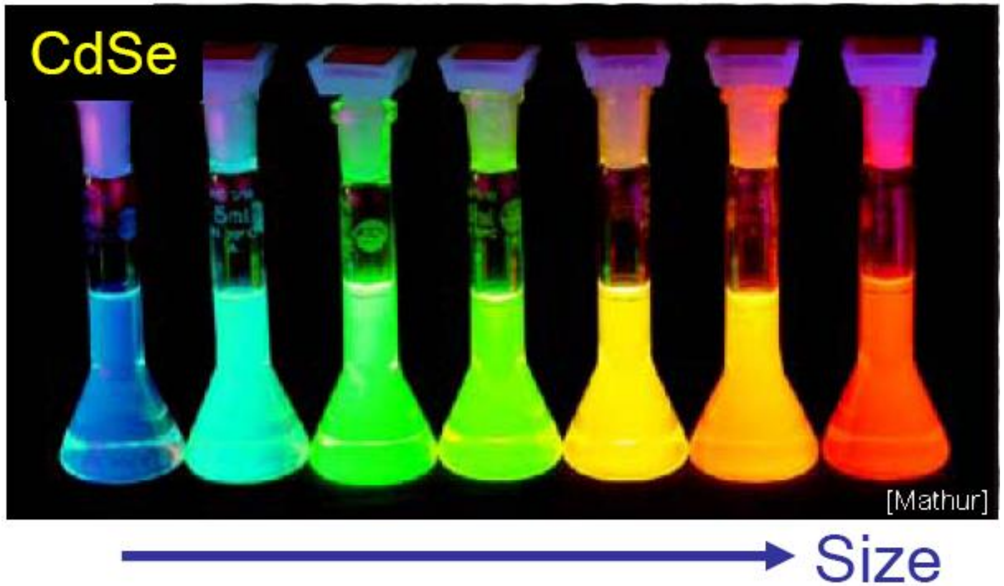
Reflexion:

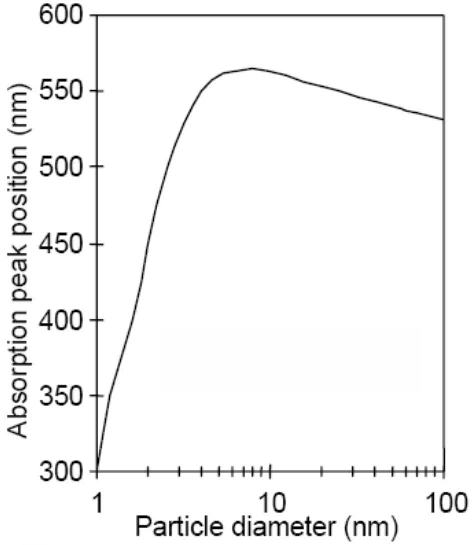



Prof. Dr. Plewa
Dr. Baur

# Optical Properties

Emission color changes with particle size



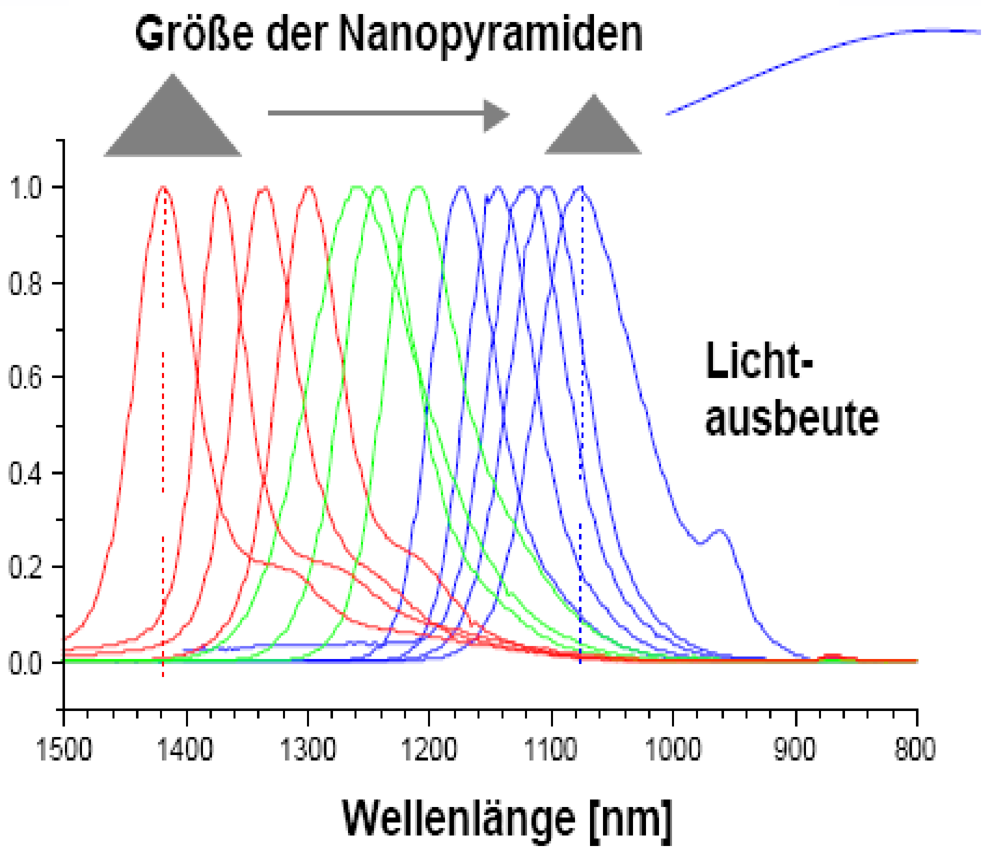



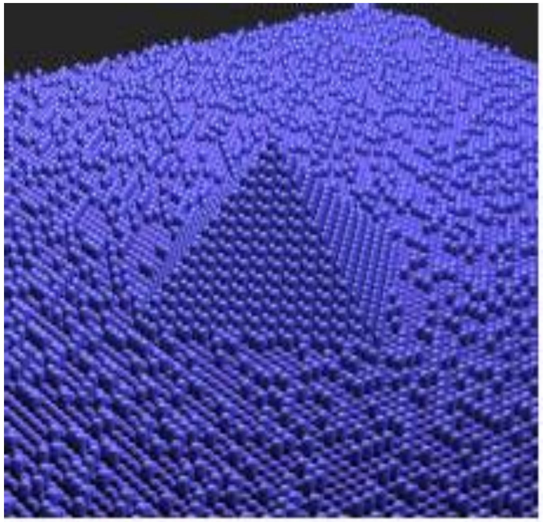
Absorption spectra of CdS particles with Increasing size.

The band gap increases with decreasing particle size

CdSe: 1.7 eV (red light) @ 20 nm
2.4 eV (blue light) @2 nm

# Optical Properties



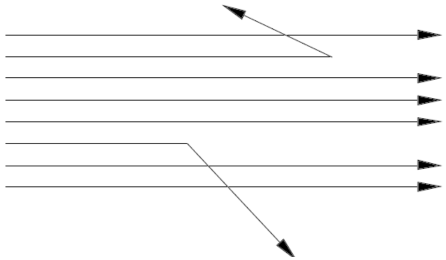



**different emission color by variation of particle size ($CdSe$ 1 - 12 nm)**

Quelle und Bilder: CC NanOp (TU Berlin)

# Optical Properties

Scattering results in a weakening of the scattered light in the direction of propagation of the light



Scattering of individual wavelengths

**Interaction between light and matter**

small particles d << $\lambda$ - ***RAYLEIGH-scattering*** *(elastical scattering)*

***violet light (400 nm) is $2^4$ = 16 times stronger scattered than red light (800 nm)***

**Example:**

- **Setting/rising sun appears red**
- **structures on the horizon appear blue**
- **the sky appears blue, not black as blue light is scattered towards the observer**

larger particles d > $\lambda$: - ***TYNDALL- scattering*** (d > $\lambda$) **or *MIE-scattering* (d ≈ $\lambda$) – only very slight wavelength dependence, appears white**

**Example:**

- **Milk**
- **Soap water**
- **Droplets of oil in water**
- **Foam**
- **fine powder (salt, snow, gypsum), which are transparent in bulk**

# Optical Properties

*Rayleigh* formula

Intensity of scattering is proportional to the wavelength by $I_{scatt} \sim \lambda^{-4}$

Intensity of scattering is linear proportional to the number of particles $I_{scatt} \sim N$

$$I_{scatt} = N \cdot \frac{I_0 \alpha^2 \pi^2}{\varepsilon_0^{\,2} \lambda^4 r^2}$$

$I_0$ Intensität des Primärlichts

$\alpha$ Polarisierbarkeit des Teilchens

$\varepsilon_0$ die elektrische Feldkonstante

*r* Abstand vom Dipolzentrum

If a material absorbs 100% light across the whole visible-light, it shows a completely black color. If only certain percentage across the entire visible-light region is equally absorbed, it is partially black or gray. If no light is absorbed across the entire visible-light region, the color is white. If the light across the entire visible-light region is not equally absorbed, certain color (e.g., yellow, brown, green) will be observed.

# Optical Properties

The intensity of the scattered light depends on:
- wavelength of incident light
- angle between incident and scattered light
- particle morphology
- physical properties of the substance

The dependence of the intensity of the scattered light on the particle size can be divided in three parts:

$$\alpha = \frac{2 \cdot \pi \cdot r}{\lambda}$$

r – particle radius, λ – wavelength of incident light

**1. Case: α > 10 and λ << r** : Light diffraction dominates (Fraunhofer equation)

**2. Case: 0,1 < α < 10 and λ ≈ r :** MIE – scattering (only slightly wavelength dependent)

**3. Case: α << 1 and λ >> r** : RAYLEIGH- scattering

$$\frac{I}{I_0} \sim \frac{r^6}{\lambda^4}$$

Small particles result in less scattering and small wavelengths are scattered more strongly

# Optical Properties

**Nano scale phosphors**

The surface is usually either amorphous or can be seen as a defect:

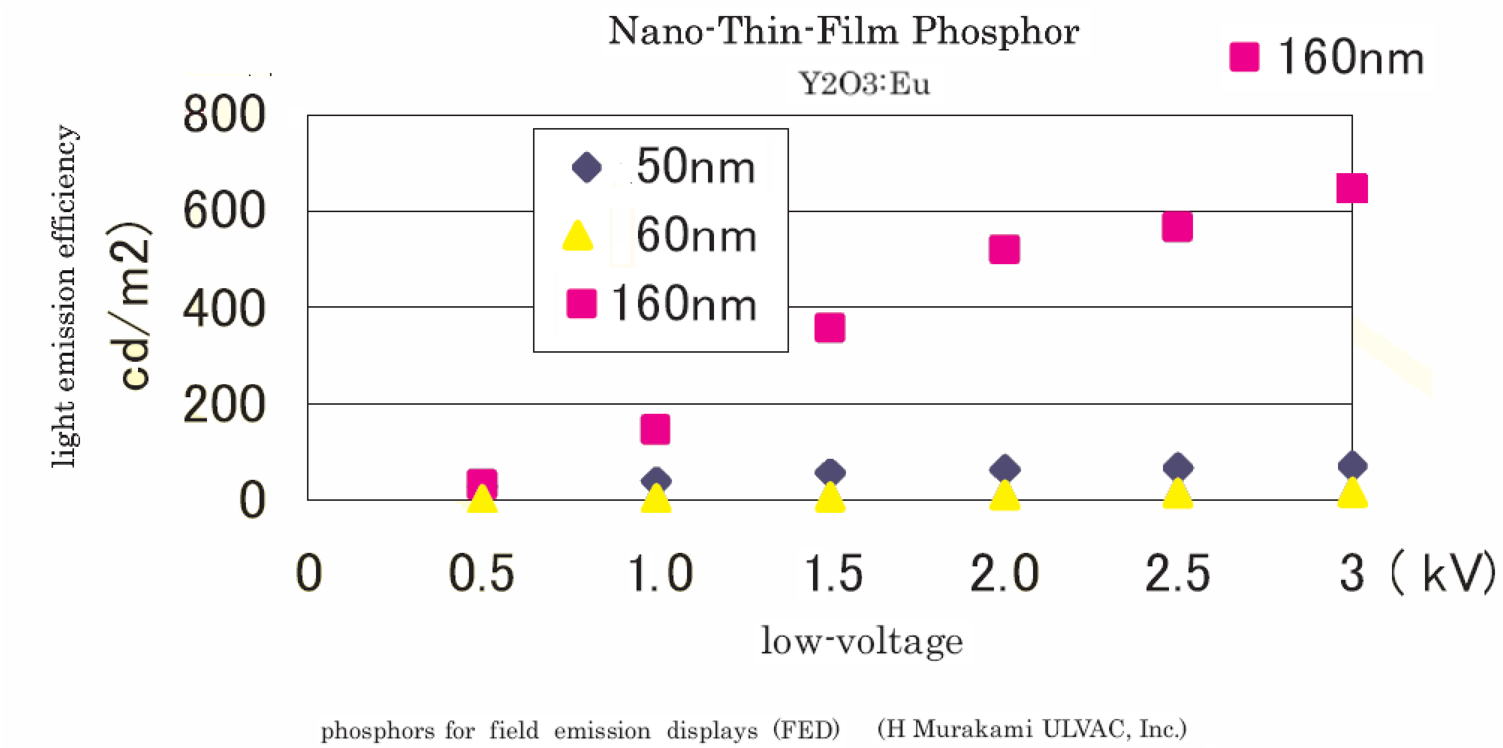
- the larger the surface area the higher the number of defects

Nano particles (1 to 100 nm) have a quantum yield of approximately 20%!

Some applications require nano particles anyway…

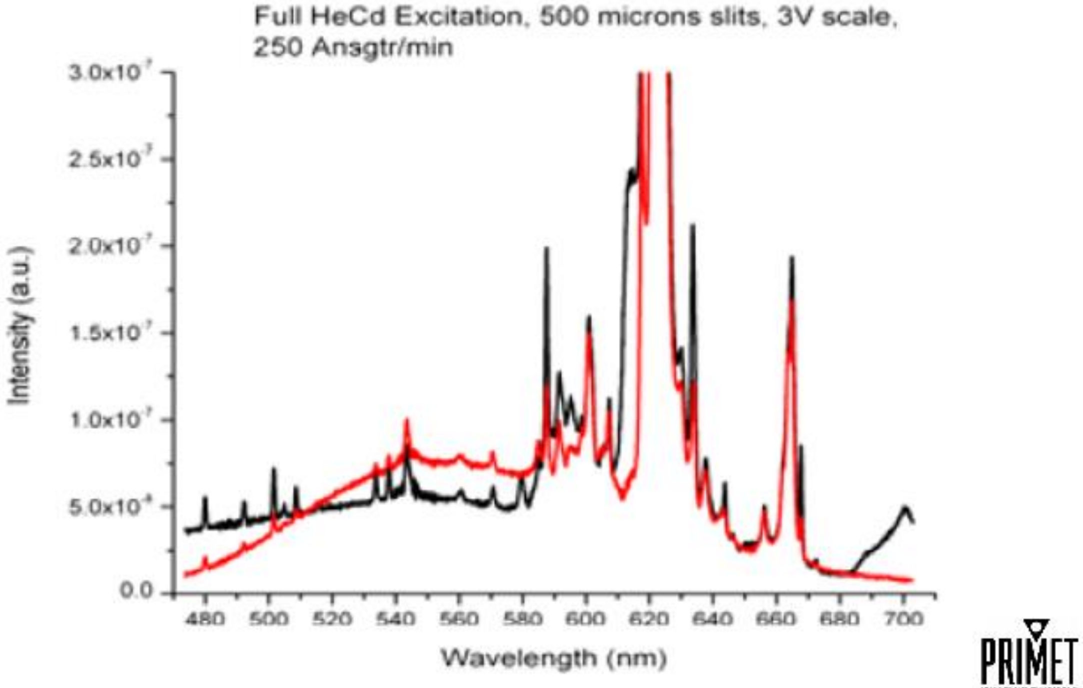
# Optical Properties

## Nano scale phosphors

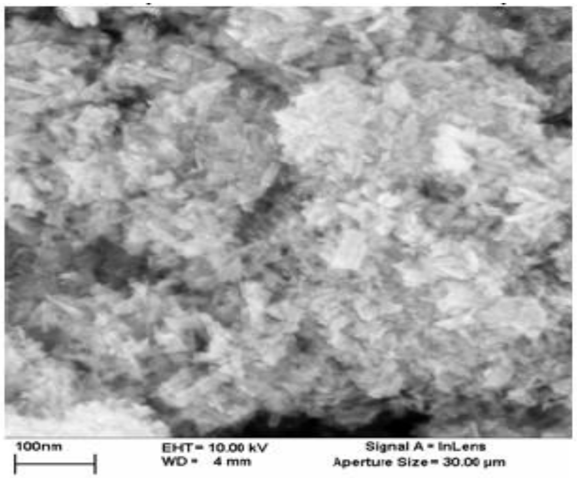


# Optical Properties

## Nano scale phosphors



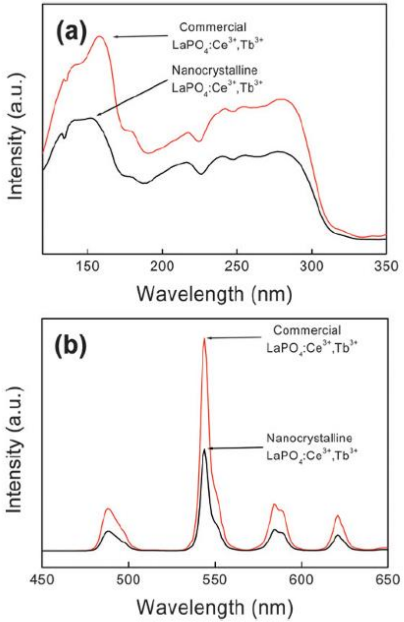

Primet GaN nanoparticles (red) show a 20% increase in intensity over high purity bulk GaN micron sized particles




Platelet GaN Nanopowder Synthesized by Primet

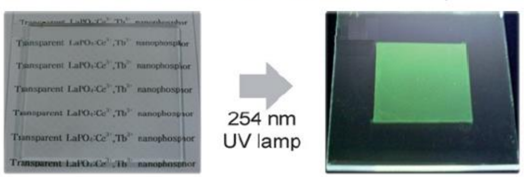
# Optical Properties

## nano scale phosphors

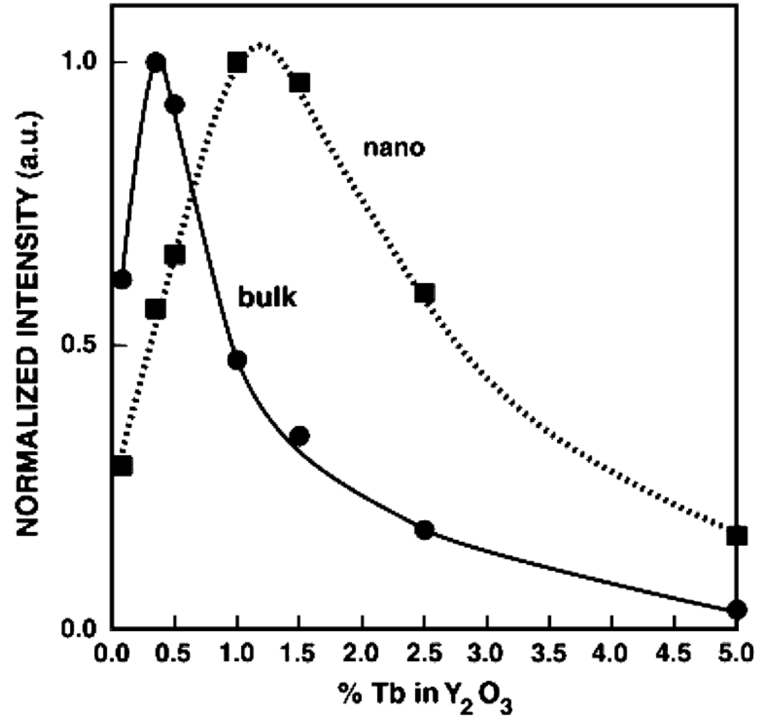



Comparison of (a) VUV excitation and (b) emission spectra of 1000 °C-annealed $La_{0.4}PO_4:Ce_{0.4},Tb_{0.2}$ nanophosphor and commercial $LaPO_4:Ce,Tb$ bulk phosphor. The excitation and emission spectra were collected with a detection wavelength of 544 nm and an excitation wavelength of 157 nm, respectively.

Woo-Seuk Song, *J. Mater. Chem.*, 2010, **20**, 6929–6934 | 6931




Nanophosphors

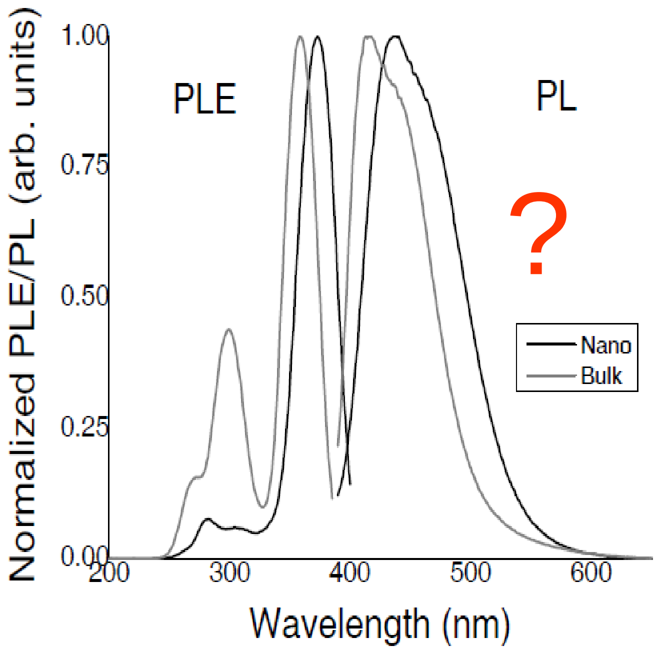



Quenching curves of nanopowder and bulk Y2O3 doped with different Tb oncentrations.[*Jacobsohn]*

# Optical Properties

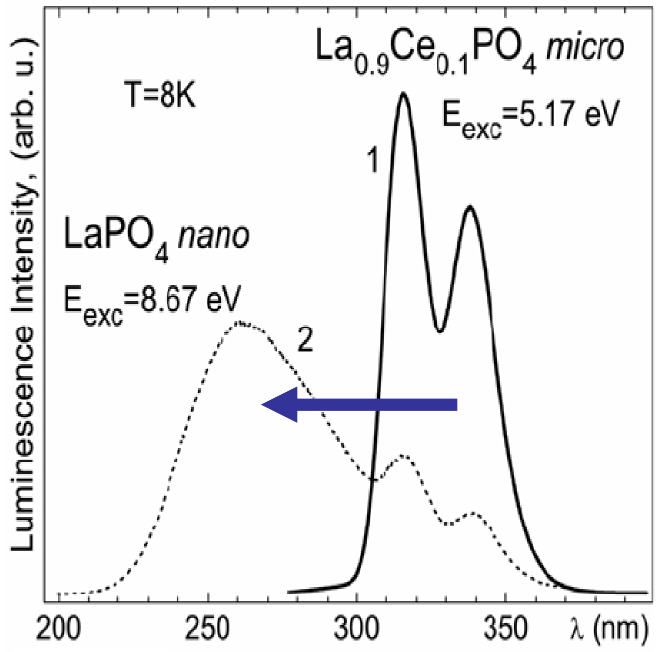
**nano scale phosphors**

Ce-doped $Lu_2SiO_5$
red-shift and enhanced Stokes shift




Normalized PLE (left curve) and PL (right curve) for nanophosphor LSO (1 % Ce) and bulk LSO.

Michael Wayne Blair 2008



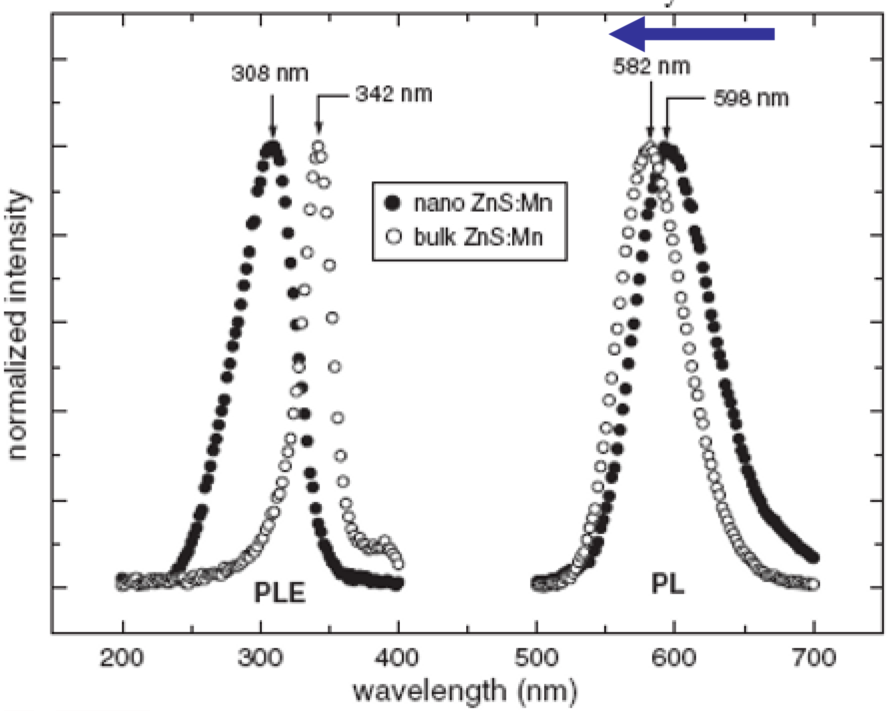

: emission spectra of $La_{0.9}Ce_{0.1}PO_4$ microphosphor (1) and nanosized $LaPO_4$ (2).

*G.Stryganyuk*

# Optical Properties

## nano scale phosphors

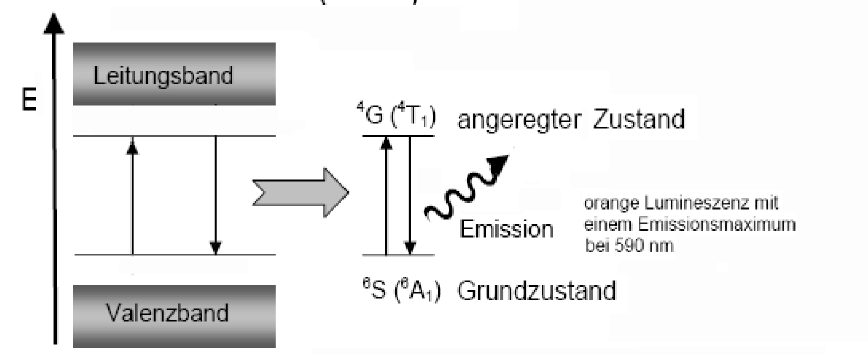
red shift for emission from nanocrystals.




PL excitation and emission spectra of ZnS:Mn 'bulk' (micrometer) and nanocrystalline (3–4 nm) powders. The maximum PL emissions occur at 582 and 598 nm for 'bulk' (micrometer size powder) and nanocrystals, respectively. The excitation maxima for PL emission are 342 and 308 nm for 'bulk' and nanocrystals, respectively.

H. Yang et al., *J. Appl. Phys.* 93, 588 (**2003**). © 2003,

Zentrenlumineszenz (ZnS:Mn)

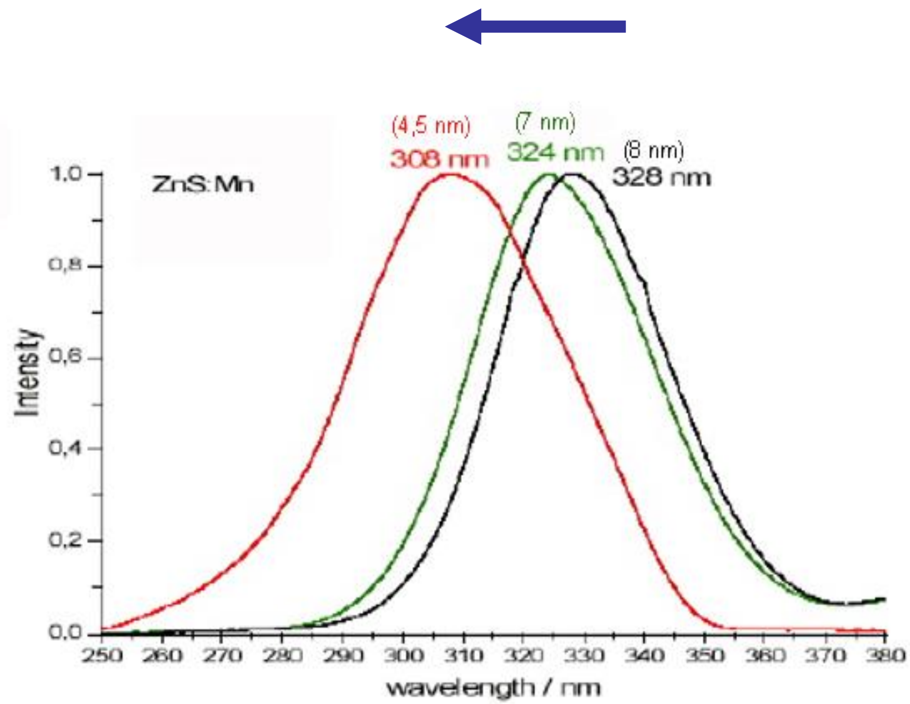



Lumineszenzmechanism im ZnS:Mn

| | | | |
|---|---|---|---|
| if $d_n$ | ↘ | then $E_g$ | ↗ |
| λ(Absorption) | ↘ | red → blue | |
| λ(Emission) | ↘ | red → blue | |
| λ(Reflection) | ↗ | blue → red | |

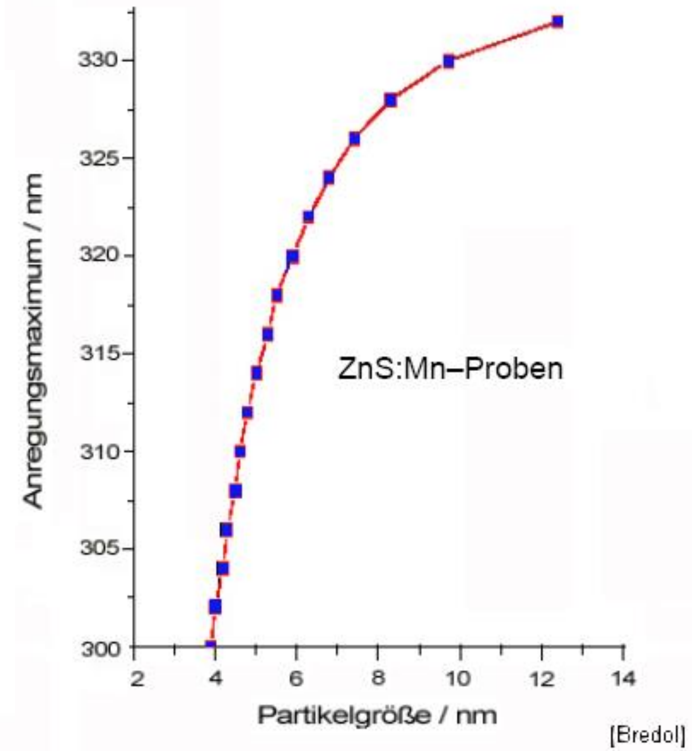
# Optical Properties

## nano scale phosphors




Anregungsspektren von ZnS:Mn–Proben unterschiedlicher Teilchengröße im Bereich unterhalb von 10 nm, angegeben sidn Peak–Wellenlängen

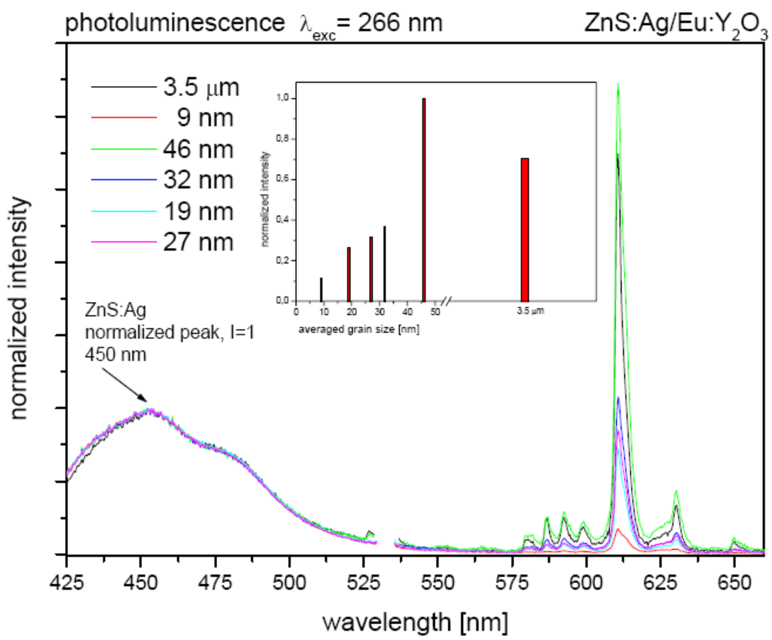
[Bredol]



# Optical Properties

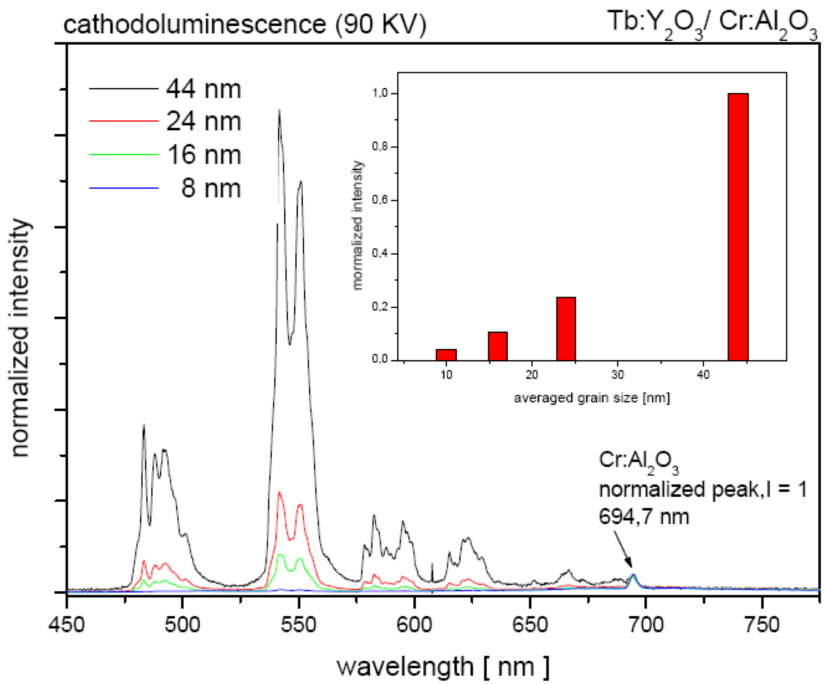
**nano scale phosphors**

Luminescent nanocrystals (nanophosphors) can offer increased luminescence efficiency under certain circumstances:




A comparison of photoluminescence ($\lambda_{exc}$ = 266 nm) of $Eu:Y_2O_3/ZnS:Ag$ blend with different sizes of $Eu:Y_2O_3$ nanocrystallites.

Piotr Psuja, Dariusz Hreniak and Wieslaw S




A comparison of cathodoluminescence (90 kV) of $Tb:Y_2O_3/Cr:Al_2O_3$ blends with different size of $Tb:Y_2O_3$ nanocrystallites

Piotr Psuja, Dariusz Hreniak and Wieslaw Strek